APPENDIX A: CALCULATION OF DIVARIANT PHASE RELATIONS

The system of equilibrium conditions in the divariant region $\alpha+\beta$ consists of equations (*cf.* equation (2-3)) of the form:

$$\begin{cases} \overline{G}^{\alpha}_{Mg_2SiO_4} = \overline{G}^{\beta}_{Mg_2SiO_4} \\ \overline{G}^{\alpha}_{Fe_2SiO_4} = \overline{G}^{\beta}_{Fe_2SiO_4} \, . \end{cases}$$

We may define difference functions, F, such that:

$$F_i^{\alpha\beta} \equiv \overline{G}_i^{\alpha} - \overline{G}_i^{\beta} \, ,$$

for each component i, and we may then seek solutions to equations of the form:

$$F_i^{\alpha\beta}\left(X_1^{\alpha}, X_1^{\beta}, P, T\right) = 0 \, .$$

In the divariant region, the requisite system of equations is simply:

$$\begin{cases} F_1^{\alpha\beta}\left(X_1^{\alpha}, X_1^{\beta}, P, T\right) = 0 \\ F_2^{\alpha\beta}\left(X_1^{\alpha}, X_1^{\beta}, P, T\right) = 0 \, . \end{cases}$$

Where $X_2^{\phi} = 1 - X_1^{\phi}$ for any given phase ϕ.

To solve for the case of equilibrium involving all three phases α, β, and γ, we need only include two more equations — those involving either the α-γ or the β-γ difference functions — in this system.

In order to solve the system, we may employ Newton's method [*cf.* Gerald and Wheatley, 1984, pp. 133-139] to reduce the solution of the system of non-linear equations to iterations of solutions of systems of linear equations. We accomplish this by developing the first-order (*i.e.*, linear) Taylor series approximation [*cf.* Hurley, 1980, pp. 710-714] to each function F_i, so that:

$$\begin{cases} 0 \approx \left(F_1^{\alpha\beta}\right) + \left(\dfrac{\partial F_1^{\alpha\beta}}{\partial X_1^{\alpha}}\right) \cdot \left(X^{\alpha}_{1,new} - X^{\alpha}_{1,old}\right) + \left(\dfrac{\partial F_1^{\alpha\beta}}{\partial X_1^{\beta}}\right) \cdot \left(X^{\beta}_{1,new} - X^{\beta}_{1,old}\right) \\ 0 \approx \left(F_2^{\alpha\beta}\right) + \left(\dfrac{\partial F_2^{\alpha\beta}}{\partial X_1^{\alpha}}\right) \cdot \left(X^{\alpha}_{1,new} - X^{\alpha}_{1,old}\right) + \left(\dfrac{\partial F_2^{\alpha\beta}}{\partial X_1^{\beta}}\right) \cdot \left(X^{\beta}_{1,new} - X^{\beta}_{1,old}\right) \, , \end{cases} \quad \text{(A-1)}$$

where each function F_i and its derivatives are evaluated at the appropriate approximate root

$X_{1,\mathrm{old}}^{\phi}$.

We may use forward finite differences [*cf.* Gerald and Wheatley, 1984, pp. 233-238] for the calculation of derivatives, so that:

$$\begin{cases} \left(\dfrac{\partial F_i^{\alpha\beta}}{\partial X_1^{\alpha}}\right)_{P,T,X_{1,\mathrm{old}}^{\beta}} \approx \dfrac{F_i^{\alpha\beta}\left(X_{1,\mathrm{old}}^{\alpha}+\delta,\, X_{1,\mathrm{old}}^{\beta},\, P,\, T\right) - F_i^{\alpha\beta}\left(X_{1,\mathrm{old}}^{\alpha},\, X_{1,\mathrm{old}}^{\beta},\, P,\, T\right)}{\delta} \\ \left(\dfrac{\partial F_i^{\alpha\beta}}{\partial X_1^{\beta}}\right)_{P,T,X_{1,\mathrm{old}}^{\alpha}} \approx \dfrac{F_i^{\alpha\beta}\left(X_{1,\mathrm{old}}^{\alpha},\, X_{1,\mathrm{old}}^{\beta}+\delta,\, P,\, T\right) - F_i^{\alpha\beta}\left(X_{1,\mathrm{old}}^{\alpha},\, X_{1,\mathrm{old}}^{\beta},\, P,\, T\right)}{\delta} \end{cases},$$

where δ is some small finite perturbation parameter.

The linear systems (A-1) may be solved by a matrix method, such as Gaussian elimination employing partial pivoting [*cf.* Gerald and Wheatley, 1984, pp. 88-95]. Each solution of a system such as (A-1) will give the correction factors $(X_{1,\mathrm{new}}^{\phi} - X_{1,\mathrm{old}}^{\phi})$ by which the previous approximate solution $X_{1,\mathrm{old}}^{\phi}$ must be modified, and hence values for $X_{1,\mathrm{new}}^{\phi}$ may be obtained for all pertinent phases ϕ. These corrections may be applied iteratively until the absolute differences between consecutive solutions fall below some arbitrary tolerance value. Note that, when solving the univariant problem for three coexisting phases numerically, it may be necessary to scale the pressure variable to the same order of magnitude as the composition (mole fraction) variables (*i.e.*, order 10^{-1}) in order to avoid forming a nearly singular matrix during linearization.

Initial estimates of the solution variables for Newton's method may be obtained as follows. The partial molar free energy of Mg_2SiO_4 in the α phase is given by:

$$\overline{G}_{Mg_2SiO_4}^{\alpha} = G_{Mg_2SiO_4}^{\alpha}(T) + \int_1^P V_{Mg_2SiO_4}^{\alpha}\,dP' + RT \ln a_{Mg_2SiO_4}^{\alpha} \,. \qquad \text{(A-2)}$$

In equation (A-2), $G_{Mg_2SiO_4,T}^{\alpha}$ refers to the free energy of pure Mg_2SiO_4 in the α phase at temperature T and 1 bar. Equilibrium between α and β phases gives the conditions:

$$\begin{cases} \overline{G}^{\beta}_{Mg_2SiO_4} - \overline{G}^{\alpha}_{Mg_2SiO_4} = \Delta G^{\alpha\to\beta}_{Mg_2SiO_4} = 0 \\ \overline{G}^{\beta}_{Fe_2SiO_4} - \overline{G}^{\alpha}_{Fe_2SiO_4} = \Delta G^{\alpha\to\beta}_{Fe_2SiO_4} = 0\ . \end{cases}$$

Upon constructing equations similar to (A-2) for the β phase and for the Fe_2SiO_4 components, the above may be expanded to give:

$$\begin{cases} \Delta G^{\alpha,\beta}_{Mg_2SiO_4} = \Delta G^{\alpha,\beta}_{Mg_2SiO_4}(T) + \int_1^P \Delta V^{\alpha,\beta}_{Mg_2SiO_4} dP' + RT \ln \kappa^{\alpha\to\beta}_{Mg_2SiO_4} = 0 \\ \Delta G^{\alpha,\beta}_{Fe_2SiO_4} = \Delta G^{\alpha,\beta}_{Fe_2SiO_4}(T) + \int_1^P \Delta V^{\alpha,\beta}_{Fe_2SiO_4} dP' + RT \ln \kappa^{\alpha\to\beta}_{Fe_2SiO_4} = 0\ , \end{cases} \tag{A-3}$$

where the equilibrium constants (the $\kappa_i^{\alpha\to\beta}$'s) are given by:

$$\begin{cases} \kappa^{\alpha\to\beta}_{Mg_2SiO_4} \equiv \dfrac{a^{\beta}_{Mg_2SiO_4}}{a^{\alpha}_{Mg_2SiO_4}} \\ \kappa^{\alpha\to\beta}_{Fe_2SiO_4} \equiv \dfrac{a^{\beta}_{Fe_2SiO_4}}{a^{\alpha}_{Fe_2SiO_4}}\ . \end{cases}$$

We may begin by assuming an ideal single-site binary solid solution (*i.e.*, $a_i^{\phi} = X_i^{\phi}$), so that:

$$\begin{cases} \kappa^{\alpha\to\beta}_{Mg_2SiO_4} = \dfrac{X^{\beta}_{Mg_2SiO_4}}{X^{\alpha}_{Mg_2SiO_4}} \\ \kappa^{\alpha\to\beta}_{Fe_2SiO_4} = \dfrac{X^{\beta}_{Fe_2SiO_4}}{X^{\alpha}_{Fe_2SiO_4}} = \dfrac{1-X^{\beta}_{Mg_2SiO_4}}{1-X^{\alpha}_{Mg_2SiO_4}}\ . \end{cases}$$

Upon solving these two equations in two unknowns (the $X^{\phi}_{Mg_2SiO_4}$'s), we obtain:

$$\begin{cases} X^{\alpha}_{Mg_2SiO_4} = \dfrac{\kappa^{\alpha\beta}_{Fe_2SiO_4}-1}{\kappa^{\alpha\beta}_{Fe_2SiO_4}-\kappa^{\alpha\beta}_{Mg_2SiO_4}} \\ X^{\beta}_{Mg_2SiO_4} = X^{\alpha}_{Mg_2SiO_4} \cdot \kappa^{\alpha\beta}_{Mg_2SiO_4}\ . \end{cases} \tag{A-4}$$

We may now solve the two equations (A-3) simultaneously for the two unknown equilibrium constants (the $\kappa_i^{\alpha\to\beta}$'s) and insert these values into equations (A-4) to obtain our initial compositional estimate.

This estimation process is easily extended to four equations in four unknowns, for approximation to the solution of the case of univariant equilibrium involving all three phases, by the inclusion of suitable expressions involving $\kappa_i^{\alpha\rightarrow\gamma}$.

APPENDIX B: MINIMIZATION OF FREE ENERGY

The problem of free energy minimization is to determine the relative amounts of a set of components which define the minimum value of the Gibbs free energy of the system at a pressure and temperature of interest and a fixed bulk chemical composition. Here we examine a steepest descent method [*cf.* Storey and Van Zeggeren, 1964], which utilizes only first order derivatives, and a quasi-Newton method [*cf.* Gill et al., 1981, pp. 116-125], which utilizes second order derivatives, for computing the minimum of the Gibbs free energy function subject to the constraint of constant bulk composition. Finally, we discuss the relative practical utility of these two methods.

Steepest Descent Method

The problem is to minimize the free energy G of the system under consideration in terms of the chemical potentials $\overline{G}_i$ and amounts n_i of the N components i comprising the system, namely:

$$G \equiv \sum_{i=1}^{N} \overline{G}_i n_i = \mathit{minimum} \ . \tag{B-1}$$

The constraint of constant bulk chemical composition may be formulated in terms of the mass balance conditions:

$$\sum_{i=1}^{N} a_{ji} n_i = Y_j \ , \ \ j=1, \cdots, M \ . \tag{B-2}$$

Here we have fixed the bulk composition in terms of the fundamental oxides in the system; a_{ji} is the number of moles of oxide j in one mole of component i, and Y_j is the total number of moles of oxide j in the system. Upon introducing a search parameter λ, the differential forms of equations (B-1) and (B-2) become:

$$\frac{dG}{d\lambda} = \sum_{i=1}^{N} \overline{G}_i \frac{dn_i}{d\lambda} \ , \tag{B-3}$$

subject to:

$$\sum_{i=1}^{N} a_{ji} \frac{dn_i}{d\lambda} = 0 \ , \ \ j{=}1, \cdots, M \ , \qquad \text{(B-4)}$$

where we have used the Gibbs-Duhem equation [*cf.* Denbigh, 1981, p. 93] at constant pressure and temperature:

$$dG = \sum_{i=1}^{N} \overline{G}_i dn_i \ ,$$

in the differentiation of equation (B-1). In order to prevent the n_i from assuming nonphysical negative values, we adopt the change of variables:

$$n_i \equiv \exp(\eta_i) \ .$$

Hence, the equations (B-3) and (B-4) become:

$$\begin{cases} \dfrac{dG}{d\lambda} = \displaystyle\sum_{i=1}^{N} \overline{G}_i n_i \frac{d\eta_i}{d\lambda} \\ \displaystyle\sum_{i=1}^{N} a_{ji} n_i \frac{d\eta_i}{d\lambda} = 0 \ , \ \ j{=}1, \cdots, M \ . \end{cases}$$

At any given composition $\{n_i'\}_1^N$ (given by the values η_i'), we find the direction of steepest descent by determining the N values of the $\frac{d\eta_i}{d\lambda}$ for which $\frac{dG}{d\lambda}$ is an extremum. Upon introducing an additional normalization condition, our problem becomes:

$$\begin{cases} \dfrac{dG}{d\lambda} = \displaystyle\sum_{i=1}^{N} \overline{G}_i' n_i' \frac{d\eta_i}{d\lambda} = \textit{extremum} \\ \displaystyle\sum_{i=1}^{N} a_{ji} n_i' \frac{d\eta_i}{d\lambda} = 0 \ , \ \ j{=}1, \cdots, M \\ \displaystyle\sum_{i=1}^{N} \left(\frac{d\eta_i}{d\lambda} \right)^2 = 1 \ , \end{cases} \qquad \text{(B-5)}$$

where the $\overline{G}_i'$ represent the chemical potentials of the N components at the composition $\{n_i'\}_1^N$. Applying the method of Lagrange multipliers [*cf.* Hurley, 1980, pp. 223-228], we obtain:

$$\sum_{i=1}^{N} \overline{G}_i' n_i' \frac{d^2\eta_i}{d\lambda^2} - 2\nu \sum_{i=1}^{N} \left(\frac{d\eta_i}{d\lambda} \right) \frac{d^2\eta_i}{d\lambda^2} - \sum_{j=1}^{M} \left(\xi_j \sum_{i=1}^{N} a_{ji} n_i' \frac{d^2\eta_i}{d\lambda^2} \right) = 0 \ ,$$

for the M+1 Lagrange multipliers ν and ξ_j. We are solving for the N values of $\frac{d\eta_i}{d\lambda}$ at the composition $\{n_i'\}_1^N$; the $\frac{d^2\eta_i}{d\lambda^2}$ may take on any arbitrary values; hence we have:

$$\overline{G}_i' n_i' - 2\nu \frac{d\eta_i}{d\lambda} - \sum_{j=1}^{M} \xi_j a_{ji} n_i' = 0 \ , \quad i=1, \cdots, N \ . \tag{B-6}$$

Upon multiplying by $a_{ki}n_i'$, summing over all N components i, and applying the mass balance condition (B-4), we arrive at:

$$\sum_{j=1}^{M} \left[\sum_{i=1}^{N} a_{ki} a_{ji} \left(n_i' \right)^2 \right] \xi_j = \sum_{i=1}^{N} \overline{G}_i' a_{ki} \left(n_i' \right)^2 \ , \quad k=1, \cdots, M \ .$$

We may solve this system of M linear equations for the M unknown values of the ξ_j using such standard techniques as Gaussian elimination with partial pivoting [*cf.* Gerald and Wheatley, 1984, pp. 88-95], and from equation (B-6) we have:

$$\frac{d\eta_i}{d\lambda} = \frac{n_i'}{2\nu} \left(\overline{G}_i' - \sum_{j=1}^{M} \xi_j a_{ji} \right) \ , \quad i=1, \cdots, N \ ,$$

where ν is chosen to satisfy the normalization condition comprising the third of equations (B-5). We now repeat the above procedure, obtaining our new composition $\{\hat{n}_i\}_1^N$ from the values of $\hat{\eta}_i$ given by:

$$\hat{\eta}_i = \eta_i' + \left(\frac{d\eta_i}{d\lambda} \right) \Delta\lambda \ , \quad i=1, \cdots, N \ ,$$

where the sign and magnitude of $\Delta\lambda$ are chosen by an accurate line search technique [*cf.* Gill et al., 1981, pp. 100-102] so as to produce a sufficient decrease in the free energy G.

This procedure may be repeated iteratively until no further sufficient decrease in the free energy G can be achieved with suitable variations in composition. In practice, it is often useful to impose the mass-balance constraints (B-2) at every iteration to prevent the compositional drift which attends the use of finite values of $\Delta\lambda$.

Quasi-Newton Method

The problem is to find the compositions $\mathbf{n}_i$ at which the free energy G of the system attains a minimum:

$$G(\mathbf{n}) \equiv \overline{\mathbf{G}}^{T}\mathbf{n} = minimum \ , \tag{B-7}$$

subject to constant bulk composition formulated in terms of the mass balance constraints:

$$\mathbf{c}(\mathbf{n}) \equiv A\,\mathbf{n} - \mathbf{y} = 0 \ . \tag{B-8}$$

Here $\overline{\mathbf{G}}$ and $\mathbf{n}$ are N-element vectors whose *i*th elements are the chemical potential and number of moles, respectively, of component i; $\mathbf{y}$ is an M-element vector whose *j*th element is the total number of moles of oxide j in the system, and A is an M×N matrix whose *ij*th element is the number of moles of oxide j in one mole of component i. In order to ensure that the compositions $\mathbf{n}_i$ do not take on nonphysical negative values, we adopt the change of variables:

$$\mathbf{n}_i \equiv \exp(\eta_i) \ .$$

We now introduce a quadratic penalty function formulation [*cf.* Gill et al., 1981, p. 208], transforming equations (B-7) and (B-8) into:

$$f(\eta) \equiv G(\eta) - \theta\mathbf{c}(\eta)^{T}\mathbf{c}(\eta) = minimum \ , \tag{B-9}$$

where θ is some scalar penalty parameter. Given an initial estimate of the composition η', we expand our new objective function $f(\eta)$ in a second order Taylor series [*cf.* Hurley, 1980, pp. 710-714] about η':

$$f(\eta) \approx f(\eta') + \mathbf{g}^{T}\left(\eta - \eta'\right) + \frac{1}{2}\left(\eta - \eta'\right)^{T}H\left(\eta - \eta'\right) \ .$$

Here $\mathbf{g}$ is the gradient vector evaluated at $\eta = \eta'$:

$$\mathbf{g} \equiv \nabla f \Big|_{\eta'} \ ,$$

and H is the symmetric N×N Hessian matrix such that:

$$H_{ij} \equiv \frac{\partial^2 \mathbf{f}}{\partial\eta_i\partial\eta_j}\Bigg|_{\eta'} \ .$$

Now if H is positive definite [*cf.* Gill et al., 1981, p. 25], then the minimum of $f(\eta)$ is given by:

$$\nabla f \approx \mathbf{g} + \left(\eta - \eta'\right)H = 0 \ , \tag{B-10}$$

so that we may obtain our next compositional estimate $\hat{\eta}$ from:

$$\hat{\boldsymbol{\eta}} = \boldsymbol{\eta}' - \epsilon H^{-1}\mathbf{g} \,, \tag{B-11}$$

where ϵ is chosen by line search [*cf.* Gill et al., 1981, 100-102] so as to produce a sufficient decrease in $\mathrm{f}(\boldsymbol{\eta})$. While we may compute the gradient vector $\mathbf{g}$ at each iteration by a finite difference method [*cf.* Gerald and Wheatley, 1984, pp. 233-238], the determination of the inverse Hessian matrix H^{-1} at each iteration is an imposing computational problem. We proceed by beginning with an initial estimate Q for H^{-1}, the identity matrix I for example, and updating the second order information in Q at each iteration. Our new compositional estimate $\hat{\boldsymbol{\eta}}$ from equation (B-11) now becomes:

$$\hat{\boldsymbol{\eta}} = \boldsymbol{\eta}' - \epsilon Q\,\mathbf{g} \,.$$

Since, from equation (B-10), we have that:

$$H^{-1}\Big(\nabla \mathrm{f}\,\Big|_{\hat{\boldsymbol{\eta}}} - \mathbf{g}\Big) \approx \hat{\boldsymbol{\eta}} - \boldsymbol{\eta}' \,, \tag{B-12}$$

we correct Q for the next iteration by an "update matrix" D, namely:

$$\hat{Q} = Q + D \,,$$

such that $\hat{Q}$ also satisfies condition (B-12):

$$\hat{Q}\Big(\nabla \mathrm{f}\,\Big|_{\hat{\boldsymbol{\eta}}} - \mathbf{g}\Big) = \hat{\boldsymbol{\eta}} - \boldsymbol{\eta}' \,.$$

From the numerous possible choices [*cf.* Gill et al., 1981, pp. 117-120] for the form of D, we have chosen the Davidon-Fletcher-Powell (DFP) [Davidon, 1959; Fletcher and Powell, 1963] update formula:

$$D = \frac{\mathbf{r}\mathbf{r}^{\mathrm{T}}}{\mathbf{r}^{\mathrm{T}}\mathbf{z}} - \frac{Q\,\mathbf{z}\mathbf{z}^{\mathrm{T}}Q}{\mathbf{z}^{\mathrm{T}}Q\,\mathbf{z}} \,,$$

where:

$$\begin{aligned} \mathbf{r} &\equiv \hat{\boldsymbol{\eta}} - \boldsymbol{\eta}' \\ \mathbf{z} &\equiv \nabla \mathrm{f}\,\Big|_{\hat{\boldsymbol{\eta}}} - \nabla \mathrm{f}\,\Big|_{\boldsymbol{\eta}'} = \hat{\mathbf{g}} - \mathbf{g} \,. \end{aligned}$$

This DFP update has the property that if the initial approximation to the inverse Hessian Q is positive definite, then all subsequent updated estimates $\hat{Q}$ are also positive definite.

This procedure may be repeated iteratively until no further sufficient decrease in the objective function f($\boldsymbol{\eta}$) can be achieved with suitable variations in composition.

Relative Utility of Methods

The steepest descent method discussed above is relatively efficient in that few evaluations of the objective function are required for each determination of new compositional estimates. However, inasmuch as this method utilizes only first-order information about the objective function, it tends to behave very poorly near the solution so that a large number of iterations produce only negligible progress toward the minimum [Gill et al., 1981, pp. 103-104]. The quasi-Newton method, on the other hand, takes advantage of second-order information about the objective function. Thus it converges relatively rapidly towards a solution, even in the region near the minimum. This method, however, is relatively expensive in terms of computation, with numerous evaluations of the objective function being required for each determination of new compositional estimates. A good strategy for the implementation of these two methods, then, would be to employ the efficient steepest descent method initially and to switch to the rapidly converging quasi-Newton method in the region near the minimum.

APPENDIX C: SOLUTION OF NONLINEAR EQUATIONS

In this section we discuss the application of Newton's method [*cf.* Gerald and Wheatley, 1984, pp. 133-139] to the solution of nonlinear equations. Given a nonlinear function f(x), we wish to find a value of x such that:

$$f(x) = 0 \; . \tag{C-1}$$

If we have some estimate x' of the solution, we may expand the function f about x' in a first-order Taylor series [*cf.* Hurley, 1980, pp. 710-714]:

$$f(x) \approx f(x') + g\left(x - x'\right) \; , \tag{C-2}$$

where g is the first derivative of f evaluated at $x=x'$:

$$g \equiv \left. \frac{df}{dx} \right|_{x=x'} \; .$$

Thus, from equations (C-1) and (C-2), we have that:

$$f(x') + g\left(x - x'\right) \approx 0 \; ,$$

so that we may obtain our next estimate $\hat{x}$ of the solution from:

$$\hat{x} = x' - \frac{f(x')}{g} \; .$$

We may repeat this process iteratively and refine our compositional estimate to within some arbitrary precision.