

## Algorithmic modifications extending MELTS to calculate subsolidus phase relations

PAUL D. ASIMOW<sup>1,\*</sup> and MARK S. GHIORSO<sup>2</sup>

<sup>1</sup>Lamont-Doherty Earth Observatory, Palisades, New York 10964-8000, U.S.A.

<sup>2</sup>Department of Geological Sciences, University of Washington, Seattle, Washington 98195-1310, U.S.A.

### ABSTRACT

Algorithmic modifications to the MELTS software package are presented in order that calculations of heterogeneous phase equilibria can be performed in the subsolidus. Methods are presented for: (1) selecting an “initial guess assemblage” that satisfies the bulk composition constraints; (2) detecting saturation of new phases (including liquid) in an assemblage; (3) adding and removing phases from the assemblage without adjusting the system bulk composition; and (4) constraining the assemblage to a fixed  $f_{\text{O}_2}$ . These methods have been added to MELTS, allowing it to calculate heterogeneous phase equilibria with or without liquid, closed or open to O, and with fixed intensive variables ( $P,T$ ), ( $P,S$ ), ( $P,H$ ), or ( $V,T$ ). Applications include fractional melting calculations, metamorphic phase equilibria, and geophysical models of subsolidus regions of the Earth.

### INTRODUCTION

MELTS (Ghiorso 1994; Ghiorso and Sack 1995) is a software package developed for modeling liquid-solid phase relations in magmatic systems. The fundamental geochemical problem solved by MELTS is the calculation of an equilibrium assemblage of phases by minimization of an appropriate energy potential, subject to constraints on bulk composition; either pressure or volume; either temperature, enthalpy or entropy; and optionally  $f_{\text{O}_2}$ . From an algorithmic perspective, the liquid phase serves several special functions in MELTS that necessitate its inclusion in the stable phase assemblage. These functions need to be replaced with a more general implementation for the minimization algorithm to function in the subsolidus. In MELTS, the liquid has the special property of unlimited freedom of compositional variation within its component space. Hence, an ex nihilo “initial guess assemblage” that satisfies the bulk composition constraints is always available by attributing the entire assemblage to liquid. Likewise, the compositional freedom of the liquid phase makes it an ideal “reservoir phase” for adding or removing small amounts of a solid phase of arbitrary composition to the metastable assemblage without adjusting the system bulk composition. Furthermore, in MELTS, the number of liquid components is equal to the number of system components, so the chemical potential of any system component can be obtained by a simple algebraic transformation. The chemical potentials of the system components, in turn, are needed to detect saturation of new solid phases and determine whether to add them to the assemblage. Finally, in MELTS the  $f_{\text{O}_2}$  is determined, and for open systems buffered, using

a parameterization of the  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio in the liquid phase. Below we discuss algorithmic modifications that replace all these special functions of the liquid. This extension is useful for, among other applications, the capacity to model fractional melting without restarting from an “all liquid” initial guess after each extraction of melt or leaving a small amount of melt behind. The latest version of MELTS, incorporating subsolidus capability, is available as a Java Applet on the world wide web at <http://melts.geology.washington.edu>.

### ALGORITHMS

#### Initial guess

Finding an initial guess that satisfies the problem constraints is often the most difficult part of a multi-dimensional, constrained minimization procedure. The constraints in this case are that (1) the total amount of each oxide (i.e., system component) in the system must equal the quantity of that oxide in the prescribed bulk composition, and (2) all phases in the system have compositions within a defined stoichiometric range. In the magmatic case (i.e., liquid present), unless a previous solution is available, one can always take as an initial guess the assumption that the entire system consists of liquid (Ghiorso 1994). Bulk compositions are then limited to those within the space of liquid compositions spanned by the particular component choice. Stoichiometric constraints on solids are typically more restricting, and only in special cases is it feasible to assign the bulk composition to a single solid phase. Hence, a method is needed in the liquid-absent case for deriving initial guess solid assemblages where all solids are of appropriate stoichiometry and sum to the prescribed bulk composition. We suggest two “initial guess” methods: (1) starting with a norm calculation

\* E-mail: [asimow@ldeo.columbia.edu](mailto:asimow@ldeo.columbia.edu)

and (2) starting with a metastable liquid. The former is more efficient, the latter is more general.

The problem of assigning a bulk composition in oxide weight percent to a set of mineral components is a familiar one to petrologists. The CIPW norm calculation (Cross et al. 1902) is the best known, but a similar procedure can be defined for any set of phases and phase components (Currie 1991). In an appendix, we give a set of rules that can be used to partition any peridotitic and many basaltic compositions into two pyroxenes, olivine or quartz, and between one and three of feldspar, garnet, and spinel. The end-member mineral components involved are those used by MELTS for these phases. The initial guess produced by a norm calculation of this kind can be tailored to include (if known) phases that are stable at equilibrium, which saves considerable computation time. In general, however, this norm calculation procedure simply produces an entry point to a minimization algorithm that must be further equipped with the means to add and drop additional phases as needed.

When the bulk composition is outside the range expressible by positive amounts of normative constituents, it is best to use a completely molten system as the initial guess. If the equilibrium assemblage is unknown, this may in fact be a more efficient approach than a "norm initial guess" containing phases that will subsequently have to be dropped. It is also likely to be more efficient than any mathematical procedure for assigning initial guesses that lacks petrological insight. Constrained minimization proceeds according to the method used in MELTS (Ghiorso and Sack 1995), adding saturated phases one at a time, until the liquid is exhausted. At this point, assuming a method is available to partition the mass contained in the last trivial batch of liquid into the available solids (see below), one arrives at an assemblage of solid phases that meets the bulk composition and phase stoichiometry constraints. This is a valid initial guess for further minimization in the subsolidus. It often produces, at the point of liquid exhaustion, an assemblage quite close to the equilibrium assemblage. Note that this procedure can be applied with some confidence at quite low temperatures, as long as the liquid thermodynamic solution model can be extrapolated into the glass state, well below the calibrated range of temperature.

It is possible to define general algorithmic procedures for assigning bulk compositions to solid phases, but without the application of petrologic constraints, such a method will not produce an initial guess as useful as either of the above methods.

### Detecting phase saturation

Ghiorso (1994) describes a method for detecting the saturation of single or multicomponent ideal or non-ideal solids with respect to a liquid phase. This method uses the chemical potentials of the liquid components as a reference for the solids to be tested. It is straightforward to extend the method to any solid assemblage

on the condition that this assemblage is in (at least metastable) heterogeneous equilibrium. Hence we require the potential minimization step of the equilibrium-seeking procedure to reach convergence with the initial solid assemblage before we test for the saturation of additional phases. In practice this is not a significant difficulty.

Our modified algorithm requires the chemical potential of each of  $nc$  system components in the solid assemblage. Let the solid assemblage contain  $m$  phase components (when two or more phases of the same mineral coexist, its components need only be counted once in this procedure). The stipulation that the assemblage be in heterogeneous equilibrium translates into a requirement that the chemical potentials of the system components are equal in all the phases. These chemical potentials are obtained from the solution of an over-constrained but consistent least-squares problem (if each system component is present in exactly one solid, then the matrix of the least squares problem is square). Let the vector  $\mu_{sol}$  of length  $m$  contain the chemical potentials of the  $m$  solid phase components present in the assemblage. We construct the  $m$  by  $nc$  matrix  $T_{sys}$  whose rows contain the stoichiometric coefficients that transform the phase components into the system components. The vector of chemical potentials of system components  $\mu_{sys}$  is obtained by solving

$$T_{sys}\mu_{sys} = \mu_{sol}. \quad (1)$$

Although this system is generally over-constrained, it has a unique exact solution if the conditions of heterogeneous equilibrium are exactly satisfied. The solution to Equation 1 is best obtained from the singular value decomposition (SVD) of  $T_{sys}$  (Lawson and Hanson 1974; Press et al. 1992).

To clarify the definitions above, consider a simple example in the system  $MgO-FeO-SiO_2$  ( $m = 3$ ). Let us allow the phases olivine, pyroxene, and quartz to be present in the equilibrium phase assemblage with the  $nc = 5$  phase components  $Mg_2SiO_4$ ,  $Fe_2SiO_4$ ,  $MgSiO_3$ ,  $FeSiO_3$ , and  $SiO_2$ . Then Equation 1 for this example reduces to

$$\begin{bmatrix} 2 & 0 & 1 \\ 0 & 2 & 1 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mu_{MgO} \\ \mu_{FeO} \\ \mu_{SiO_2} \end{bmatrix} = \begin{bmatrix} \mu_{Mg_2SiO_4}^{Olivine} \\ \mu_{Fe_2SiO_4}^{Olivine} \\ \mu_{MgSiO_3}^{Pyroxene} \\ \mu_{FeSiO_3}^{Pyroxene} \\ \mu_{SiO_2}^{Quartz} \end{bmatrix}. \quad (2)$$

If  $\mu_{sys}$  is further transformed into the chemical potentials of  $nc$  liquid components ( $\mu_{liq}$ ), a fictive liquid is then sufficiently characterized to use the saturation algorithm of Ghiorso (1994) without further modification. Indeed, this method may be used as presented to detect the saturation of non-ideal liquids with respect to subsolidus assemblages.

### Adding and removing phases

In the implementation of MELTS described by Ghiorso and Sack (1995), when a newly saturated phase is recognized or some solid phase undergoes exsolution, a tiny mass of the new phase is added by subtracting from the liquid the needed mass of each liquid component in order to make up the desired solid composition. Similarly, during the course of potential minimization, when the mass of a solid drops to a (smaller) “tiny” level, it is removed by adding the appropriate amount of each component to the liquid to conserve bulk composition. The compositional flexibility of the liquid phase makes this procedure trivial in both cases. When liquid is absent, however, more care is required. Two methods present themselves. In the first, negligible changes in the bulk composition are allowed. If the mass of phases added or dropped is sufficiently small, the change in bulk composition implied by simply adding or removing the components contained in the solid from the system bulk composition may be negligible. When performing calculations near a phase boundary, however, the unpredictability and path dependence of this procedure are unacceptable. Consequently, we prefer to use a second method, described below, which exactly satisfies the original bulk composition constraints.

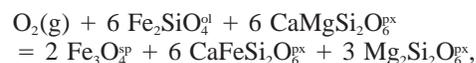
This procedure is essentially a general method for assigning a bulk composition to phase components, but as the masses involved represent small perturbations to an assemblage already near (metastable) equilibrium, the arbitrary nature of the assignment is not a disadvantage. Let  $j$  denote the phase to be added or dropped. The composition of the phase is represented by the signed number of moles of its phase components (positive if the phase is being added, negative if it is being dropped) arranged as a vector  $\delta\mathbf{m}_j$  of length  $na_j$ . We begin by transforming  $\delta\mathbf{m}_j$  into the  $nc$  system components:  $\delta\mathbf{m}_{\text{sys}} = \mathbf{T}_j\delta\mathbf{m}_j$ , where the  $nc \times na_j$  stoichiometry matrix  $\mathbf{T}_j$  is a submatrix of  $\mathbf{T}_{\text{sys}}$ , defined above. Let us say that the remaining assemblage after phase  $j$  is dropped or the pre-existing assemblage to which phase  $j$  is to be added contains  $n_{\text{sol}}$  phase components (here we count coexisting phases of the same mineral as independent phase components in order to minimize the perturbation). We seek a vector  $\delta\mathbf{m}_{\text{sol}}$  of perturbations to the number of moles of each phase in the assemblage. If  $\mathbf{T}_{\text{sol}}$  is the  $nc \times n_{\text{sol}}$  stoichiometry matrix that transforms the system components of the assemblage to the set of phase components we seek to modify ( $\mathbf{T}_{\text{sol}} = \mathbf{T}_{\text{sys}}^T$ ), then the solution is expressed by the system of linear equations  $\mathbf{T}_{\text{sol}}\delta\mathbf{m}_{\text{sol}} = \delta\mathbf{m}_{\text{sys}}$  that is, in general, underconstrained, i.e., there is an  $(n_{\text{sol}} - nc)$  dimensional space of solutions all of which satisfy the constraints. Solution of this system by SVD will produce the solution vector  $\delta\mathbf{m}_{\text{sol}}$  that has the smallest 2-norm [i.e., the member of the solution family with minimum  $(\delta\mathbf{m}_{\text{sol}}^T \delta\mathbf{m}_{\text{sol}})^{1/2}$ ]. It is possible to take advantage of this property, and to choose instead the solution that least perturbs the assemblage. The smallest relative perturbation to the assem-

blage is obtained by transferring as much mass as possible from the most abundant phase components in the assemblage and as little mass as possible from the least abundant phase components. The SVD can be forced to choose this solution by weighting the rows of  $\mathbf{T}_{\text{sol}}$  as follows: let  $\mathbf{m}_{\text{sol}}$  be the vector of total abundances of the  $n_{\text{sol}}$  phase components in the assemblage to be perturbed, and denote the  $n_{\text{sol}} \times n_{\text{sol}}$  diagonal matrix with  $\mathbf{m}_{\text{sol}}$  on the main diagonal as  $\mathbf{M}_{\text{sol}}$ . Since the matrix is diagonal, its inverse is simply the diagonal matrix with the reciprocal of each element of  $\mathbf{m}_{\text{sol}}$  along its diagonal. Then we have  $[\mathbf{T}_{\text{sol}} \cdot \mathbf{M}_{\text{sol}}] \cdot [\mathbf{M}_{\text{sol}}^{-1} \cdot \delta\mathbf{m}_{\text{sol}}] = \delta\mathbf{m}_{\text{sys}}$ , which we solve using the SVD of  $[\mathbf{T}_{\text{sol}} \cdot \mathbf{M}_{\text{sol}}]$ . This yields on backsubstitution the particular solution  $[\mathbf{M}_{\text{sol}}^{-1} \cdot \delta\mathbf{m}_{\text{sol}}]$  with the smallest 2-norm. The least-squares constraint on the particular solution thereby acts most strongly on the elements of this vector that have been weighted to large values by dividing by small elements of  $\mathbf{m}_{\text{sol}}$ . The desired solution is then obtained simply by premultiplying the particular solution by  $\mathbf{M}_{\text{sol}}$ , which recovers the desired solution vector  $\delta\mathbf{m}_{\text{sol}}$ .

Even though this method is intended to make small perturbations to the assemblage, it is possible for it to fail by overstepping the stoichiometry limits on one or more phases. Should this occur, the calculation can always be resumed by returning to the initial guess methods documented above.

### Measuring and buffering $f_{\text{O}_2}$

In order to perform calculations at constrained  $f_{\text{O}_2}$ , like other constraints, it must be correct in the initial guess to each constrained minimization step, so an auxiliary algorithm is needed to buffer  $f_{\text{O}_2}$  to the desired value before minimization (and to calculate  $f_{\text{O}_2}$  in unconstrained calculations). The algorithms of Ghiorso and Sack (1995) accomplish this task using the parameterization of Kress and Carmichael (1991) for estimating  $\text{Fe}_2\text{O}_3/\text{FeO}$  in silicate liquids as a function of composition, temperature, pressure, and  $f_{\text{O}_2}$ . In the absence of a liquid, a method is required that enforces the  $f_{\text{O}_2}$  buffer on the whole assemblage rather than in the liquid phase. For particular mineral assemblages, this is straightforward; the challenge is to find a general method that works for any  $\text{Fe}^{3+}$ - and  $\text{Fe}^{2+}$ -bearing mineral assemblage. Let us first consider the case of an assemblage of spinel, olivine, and pyroxene. In this case we can write a balanced redox reaction:



which can be expressed as

$$\sum_{i=1}^6 n_i m_i = 0, \quad (3)$$

where  $i = 1$  refers to  $\text{O}$ ,  $n_i$  are stoichiometric coefficients (negative for reactants, positive for products), and  $m_i$  are molar quantities of the reactant and product phase components. The reaction is characterized by the equilibrium constant

$$K = \frac{(a_{Mn}^{sp})^2 (a_{Hd}^{px})^6 (a_{En}^{px})^3}{(a_{Fa}^{ol})^6 (a_{Di}^{px})^6 f_{O_2}} = \exp(-\Delta G^0/RT), \quad (4)$$

where  $a$  is activity,  $R$  the gas constant,  $T$  the absolute temperature, and  $\Delta G^0$  the standard-state Gibbs free energy of reaction. Hence at equilibrium,

$$RT \ln f_{O_2} = \Delta G^0 + RT \ln \left( \frac{(a_{Mn}^{sp})^2 (a_{Hd}^{px})^6 (a_{En}^{px})^3}{(a_{Fa}^{ol})^6 (a_{Di}^{px})^6} \right) \quad (5)$$

or more generally

$$RT \ln f_{O_2} = \sum_{i=1}^6 n_i g_i^0 + RT \sum_{i=2}^6 n_i \ln a_i, \quad (6)$$

where  $g_i^0$  is the standard-state molar free energy of phase component  $i$ ,  $a_i$  is the activity of phase component  $i$  in the appropriate phase, and the sum over activities excludes O ( $i = 1$ ). All the derivatives of  $f_{O_2}$  with respect to intensive variables can be obtained from this expression. Buffering the system to a prescribed  $f_{O_2}$  simply requires forcing the reaction toward or away from oxygen until the activities of the components change so as to yield the correct  $f_{O_2}$ .

Following this example as a model, it is clear that a general technique is required for finding a balanced redox reaction among the  $m$  phase components actually present in the assemblage plus  $O_2$ ; once such a reaction is found, the procedure for calculating  $f_{O_2}$  is identical to that for the spinel-pyroxene-olivine oxybarometer above. We proceed as follows: construct a right-hand-side vector  $\delta \mathbf{m}_{\text{sys}}^*$  of length  $nc + 1$  representing the net change in moles of O and system components effected by the desired reaction, and set the values equal to the stoichiometry of the simplest redox reaction possible among the system components and O. For example, if the system components are the oxides  $SiO_2$ - $TiO_2$ - $Al_2O_3$ - $Cr_2O_3$ - $Fe_2O_3$ - $FeO$ - $MgO$ - $CaO$ - $Na_2O$ , we use the reaction  $4 FeO + O_2 = 2 Fe_2O_3$  resulting in  $\delta \mathbf{m}_{\text{sys}}^* = \{-1, 0, 0, 0, 0, 2, -4, 0, 0, 0\}$ . Note that the first position in  $\delta \mathbf{m}_{\text{sys}}^*$  represents the stoichiometric coefficient for  $O_2$ , and the rest of the vector indexes the system components in their usual order. Next we construct the  $(nc + 1) \times (m + 1)$  matrix  $\mathbf{T}_{\text{sol}}^*$ , which converts the system components plus  $O_2$  to all the solid phase components present in the assemblage plus  $O_2(g)$ . Hence if  $O_2(g)$  is the first phase and  $O_2$  the first component,

$$\mathbf{T}_{\text{sol}}^* = \begin{bmatrix} 1 & 0 & \cdots & 0 \\ 0 & & & \\ \vdots & & \mathbf{T}_{\text{sol}} & \\ 0 & & & \end{bmatrix}. \quad (7)$$

then any solution vector  $\mathbf{n}_{\text{sol}}^*$  satisfying  $\mathbf{T}_{\text{sol}}^* \cdot \mathbf{n}_{\text{sol}}^* = \delta \mathbf{m}_{\text{sys}}^*$  gives the coefficients of a balanced redox reaction

$$\sum_{i=1}^{m+1} n_{\text{sol},i}^* m_i = 0 \quad (8)$$

that adds one mole of  $O_2$  to the system while converting four moles of  $Fe^{2+}$  into  $Fe^{3+}$ . This system is undercon-

strained (there is an  $m - nc$  dimensional solution space), but we have some grounds on which to choose among the feasible solutions. If, once again, we wish to find the reaction that minimizes the perturbation to the system required to introduce or remove a given quantity of O then, proceeding as above, we construct the diagonal weighting matrix  $\mathbf{M}_{\text{sol}}^*$  and assign a large value to the first element, representing  $O_2(g)$ . Then we compute the SVD of  $[\mathbf{T}_{\text{sol}}^* \cdot \mathbf{M}_{\text{sol}}^*]$ , back-substitute to obtain the weighted particular solution  $[\mathbf{M}_{\text{sol}}^{*-1} \cdot \mathbf{n}_{\text{sol}}^*]$ , and then recover the desired reaction stoichiometry  $\mathbf{n}_{\text{sol}}^*$  by premultiplying by  $\mathbf{M}_{\text{sol}}^*$ . On the other hand, it may be desirable for computational reasons to find the simplest reaction among the feasible solutions, e.g., one involving the fewest phase components. This may be obtained by constructing a matrix whose first column is the particular solution to the unweighted SVD problem and whose other columns form an orthonormal basis for the nullspace (e.g., those columns of  $\mathbf{V}$  returned by the SVD of  $\mathbf{T}_{\text{sol}}^* = \mathbf{U} \cdot \text{diag}[\mathbf{w}] \cdot \mathbf{V}^T$  that correspond to zeroes in  $\mathbf{w}$ ), and then performing a column reduction to insert as many zeros as possible into the desired column.

## DISCUSSION

With the four modifications detailed above, the MELTS software package can be applied to a range of solid-state equilibrium problems. Brown (1996), for example, used MELTS with these subsolidus extensions to calculate density, mineral assemblages, and seismic velocities for tectonic and stable North American mantle lithosphere. Application of this method to a full range of crustal metamorphic problems will depend, however, on progress in thermodynamic models for a number of highly complex minerals. Phases such as staurolite, amphibole, chlorite, chloritoid, etc. have not yet been modeled adequately.

The algorithms developed herein, together with those of Ghiorso (1994) and Ghiorso and Sack (1995), may in principle be used to compute equilibrium assemblages at fixed  $(T, P, f_{O_2})$  as well as  $(S, P, f_{O_2})$ ,  $(H, P, f_{O_2})$ , or  $(T, V, f_{O_2})$ . This is not, however, the best way to calculate  $f_{O_2}$ -buffered isentropic, isenthalpic, or isochoric equilibria. It is unclear what these calculations represent if performed directly. Buffering of  $f_{O_2}$  explicitly requires adding or removing  $O_2$  from the system at many steps. If we enforce constant entropy, for example, this implies that the  $O_2$  entering or leaving the system is at absolute zero, since it carries no entropy. The implication is that the buffering of  $O_2$  will implicitly cool or heat the system, and this is unlikely to correspond to any meaningful physical situation. Instead we recommend a two-stage procedure that alternates between (1) steps toward equilibrium at fixed  $(S, P)$  in a closed system and (2) buffering steps where  $O_2$  is added or removed at the current temperature of the system and the reference entropy is adjusted accordingly.

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*(Appendix 1 is on next page.)*

## APPENDIX 1. A norm for subsolidus initial guesses to MELTS

A wide range of basalts and peridotites can be successfully assigned to a norm that utilizes two pyroxenes, either olivine or quartz, and at least one aluminous mineral. The following procedure is customized to produce good initial guesses for peridotites in the system  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-FeO}\pm\text{NiO-MgO}\pm\text{MnO}\pm\text{CoO-CaO-Na}_2\text{O}\pm\text{K}_2\text{O}$ , (oxides listed with “±” are optional) using the following phase components (for pyroxene components, C in the abbreviation indicates clinopyroxene, O indicates orthopyroxene):

olivine:	fayalite (Fa)	$\text{Fe}_2\text{SiO}_4$	forsterite (Fo)	$\text{Mg}_2\text{SiO}_4$
	monticellite (Mc)	$\text{CaMgSiO}_4$	tephroite (Tp)	$\text{Mn}_2\text{SiO}_4$
	Ni-olivine (NiOl)	$\text{Ni}_2\text{SiO}_4$	Co-olivine (CoOl)	$\text{Co}_2\text{SiO}_4$
pyroxene:	diopside (CDi, ODi)	$\text{CaMgSi}_2\text{O}_6$	essenite (CEs, OEs)	$\text{CaFe}^{3+}\text{AlSiO}_6$
	jadeite (CJd, OJd)	$\text{NaAlSi}_2\text{O}_6$	hedenbergite (CHd, OHd)	$\text{CaFeSi}_2\text{O}_6$
	enstatite (CEn, OEn)	$\text{Mg}_2\text{Si}_2\text{O}_6$	buffoonite (CBf, OBf)	$\text{CaMg}_{0.5}\text{Ti}_{1.5}\text{Fe}^{3+}\text{SiO}_6$
	aluminobuffoonite (CABf, OABf)		$\text{CaMg}_{0.5}\text{Ti}_{1.5}\text{AlSiO}_6$	
spinel:	hercynite (Hc)	$\text{FeAl}_2\text{O}_4$	chromite (Cr)	$\text{FeCr}_2\text{O}_4$
	spinel (Sp)	$\text{MgAl}_2\text{O}_4$	magnetite (Mt)	$\text{Fe}_3\text{O}_4$
	ulvospinel (Uv)	$\text{Fe}_2\text{TiO}_4$		
garnet:	pyrope (Py)	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	almandine (Alm)	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
	grossular (Gr)	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$		
feldspar:	albite (Ab)	$\text{NaAlSi}_3\text{O}_8$	anorthite (An)	$\text{CaAl}_2\text{Si}_2\text{O}_8$
	sanidine (Sd)	$\text{KAISi}_3\text{O}_8$		

Procedure (the term “Assign” implies a deduction ; the term “Set” does not):

Rule 0. Convert the analysis in oxides or other system components to molar abundances of oxides in 100 g of system; select from one to three aluminous phases (garnet, spinel, feldspar) to include; if  $\text{Cr}_2\text{O}_3$  is present spinel is mandatory and, if  $\text{K}_2\text{O}$  is included, feldspar is mandatory. Decide whether olivine is likely to be needed; if MnO, NiO, or CoO is present, olivine is mandatory. Quartz will be added if necessary.

Rule 1 ( $\text{Cr}_2\text{O}_3$ , MnO, NiO, CoO).

Assign all  $\text{Cr}_2\text{O}_3$  to Cr. Deduct Cr from FeO.

Assign all MnO to Tp ( $\text{Tp} = 0.5 * \text{MnO}$ ). Deduct Tp from  $\text{SiO}_2$ .

Assign all NiO to NiOl ( $\text{NiOl} = 0.5 * \text{NiO}$ ). Deduct NiOl from  $\text{SiO}_2$ .

Assign all CoO to CoOl ( $\text{CoOl} = 0.5 * \text{CoO}$ ). Deduct CoOl from  $\text{SiO}_2$ .

Rule 2 ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ). If the system contains  $\text{K}_2\text{O}$ , feldspar must be included.

Assign all  $\text{K}_2\text{O}$  to Sd ( $\text{Sd} = 2 * \text{K}_2\text{O}$ ); deduct  $0.5 * \text{Sd}$  from  $\text{Al}_2\text{O}_3$  and  $3 * \text{Sd}$  from  $\text{SiO}_2$ .

If feldspar is to be included:

Assign  $0.9 * \text{Na}_2\text{O}$  to Ab, leaving remainder for jadeite ( $\text{Ab} = 1.8 * \text{Na}_2\text{O}$ ); deduct  $0.5 * \text{Ab}$  from  $\text{Al}_2\text{O}_3$  and  $3 * \text{Ab}$  from  $\text{SiO}_2$ .

Assign  $0.66 * \text{Na}_2\text{O}$  to CJd ( $\text{CJd} = 1.32 * \text{Na}_2\text{O}$ ); deduct  $0.5 * \text{CJd}$  from  $\text{Al}_2\text{O}_3$  and  $2 * \text{CJd}$  from  $\text{SiO}_2$ .

Assign remaining  $\text{Na}_2\text{O}$  to OJd ( $\text{OJd} = 2.0 * \text{Na}_2\text{O}$ ); deduct  $0.5 * \text{OJd}$  from  $\text{Al}_2\text{O}_3$  and  $2 * \text{OJd}$  from  $\text{SiO}_2$ .

Rule 3 ( $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  in spinel).

If spinel is to be included:

Assign  $0.25 * \text{TiO}_2$  to Uv; deduct  $2 * \text{Uv}$  from FeO.

Assign  $0.4 * \text{Fe}_2\text{O}_3$  to Mt; deduct Mt from FeO.

Rule 4 ( $\text{Al}_2\text{O}_3$ ).

If spinel is to be included:

Assign  $0.5 * \text{Al}_2\text{O}_3$  to Sp; deduct Sp from MgO.

If  $(\text{Mt} + \text{Cr} + 2 * \text{Uv} - 0.2 * \text{Al}_2\text{O}_3 > 0)$  assign  $-0.2 * \text{Al}_2\text{O}_3$  to Hc (i.e., set  $\text{Hc} = -0.2 * \text{Al}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3 = 1.2 * \text{Al}_2\text{O}_3$ ) and add  $-\text{Hc}$  to FeO.

else set  $\text{Hc} = (0.001 - \text{Mt} - \text{Cr} - 2 * \text{Uv})$ , add  $-\text{Hc}$  to  $\text{Al}_2\text{O}_3$  and FeO.

If feldspar is to be included:

Assign  $0.64 * \text{Al}_2\text{O}_3$  to An; deduct An from CaO and  $2 * \text{An}$  from  $\text{SiO}_2$ .

If garnet is to be included:

Set temporary variable  $\text{TotalGt} = 0.6 * \text{Al}_2\text{O}_3$ .

Set  $\text{Alm} = \text{TotalGt} * [2.0 * \text{FeO} / (2.0 * \text{FeO} + 3.0 * \text{MgO} + 0.5 * \text{CaO})]$ ; deduct  $2 * \text{Alm}$  from FeO.

Set  $\text{Py} = \text{TotalGt} * [3.0 * \text{MgO} / (2.0 * \text{FeO} + 3.0 * \text{MgO} + 0.5 * \text{CaO})]$ ; deduct  $2 * \text{Py}$  from MgO.

Set  $\text{Gr} = \text{TotalGt} * [0.5 * \text{CaO} / (2.0 * \text{FeO} + 3.0 * \text{MgO} + 0.5 * \text{CaO})]$ ; deduct  $2 * \text{Gr}$  from CaO.

Deduct  $\text{TotalGt}$  from  $\text{Al}_2\text{O}_3$  and  $3.0 * \text{TotalGt}$  from  $\text{SiO}_2$ .

Rule 5 ( $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ). Perform all the following steps before deducting anything from  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , or  $\text{Al}_2\text{O}_3$ .

Set  $\text{OAbf} = 0.75 * (\text{Al}_2\text{O}_3 + \text{TiO}_2 - \text{Fe}_2\text{O}_3)$ .

Set  $\text{CABf} = 0.25 * (\text{Al}_2\text{O}_3 + \text{TiO}_2 - \text{Fe}_2\text{O}_3)$ .

Set  $\text{OBf} = 0.75 * (\text{Fe}_2\text{O}_3 + \text{TiO}_2 - \text{Al}_2\text{O}_3)$ .

Set  $\text{CBf} = 0.25 * (\text{Fe}_2\text{O}_3 + \text{TiO}_2 - \text{Al}_2\text{O}_3)$ .

Set  $\text{OEs} = 0.75 * (\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 - \text{TiO}_2)$ .

Set  $\text{CEs} = 0.25 * (\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 - \text{TiO}_2)$ .

Deduct  $(\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{Fe}_2\text{O}_3)$  from CaO and  $\text{SiO}_2$ .

Deduct  $\text{TiO}_2$  from MgO.

Set  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  equal to zero.

Rule 6 (CaO). Perform the following steps before modifying CaO:

Set  $\text{CHd} = 0.15 * \text{CaO}$ . Deduct CHd from FeO and  $2 * \text{CHd}$  from  $\text{SiO}_2$ .

If olivine is to be (provisionally) included, set  $\text{OHd} = \text{CaO}$ , else set  $\text{OHd} = \text{FeO}$ .

Set  $\text{ODi} = -1.05 * \text{OHd}$ .

Deduct  $(\text{CHd} + \text{OHd} + \text{ODi})$  from CaO.

Deduct ODi from MgO. Deduct OHd from FeO.

Deduct  $2 * (\text{OHd} + \text{ODi})$  from  $\text{SiO}_2$ .

If olivine is to be (provisionally) included, set  $\text{CDi} = 0.833 * \text{CaO}$ , else set  $\text{CDi} = \text{CaO}$ .

Deduct CDi from CaO and MgO. Deduct  $2 * \text{CDi}$  from  $\text{SiO}_2$ .

If  $(\text{CaO} < 0)$  the composition is infeasible. End in failure.

If olivine is to be included, assign remaining CaO to Mc and deduct Mc from MgO and  $\text{SiO}_2$ .

Rule 7 (MgO, FeO,  $\text{SiO}_2$ ).

If olivine is to be included assign remaining FeO to Fa ( $\text{Fa} = 0.5 * \text{FeO}$ ); deduct Fa from  $\text{SiO}_2$ .

If  $(\text{MgO} > \text{SiO}_2)$  and olivine is to be included, set  $\text{Fo} = (\text{MgO} - \text{SiO}_2)$ ; deduct Fo from  $\text{SiO}_2$  and  $2 * \text{Fo}$  from MgO.

Set  $\text{OEn} = 0.475 * \text{MgO}$ ; deduct  $2 * \text{OEn}$  from MgO and  $\text{SiO}_2$ .

Assign remaining MgO to CEn ( $\text{CEn} = 0.5 * \text{MgO}$ ). Deduct  $2 * \text{CEn}$  from  $\text{SiO}_2$ .

If  $(\text{SiO}_2 > 0)$ , a silica excess exists. Add quartz to the assemblage and assign all remaining  $\text{SiO}_2$  to quartz.

If any oxide is not now equal to zero, the composition is infeasible. End in defeat, or else return successfully.