Algorithmic modifications extending MELTS to calculate subsolidus phase relations

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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_{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_{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_{O_2} is determined, and for open systems buffered, using a parameterization of the Fe_2O_3/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 multidimensional, 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

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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 μ_{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 μ_{sys} is obtained by solving

$$T_{sys}\mu_{sys} = \mu_{sol}. \tag{1}$$

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$_2$SiO$_4$, Fe$_2$SiO$_4$, MgSiO$_3$, FeSiO$_3$, and SiO$_2$. Then Equation 1 for this example reduces to

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

If μ_{sys} is further transformed into the chemical potentials of nc liquid components (μ_{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.
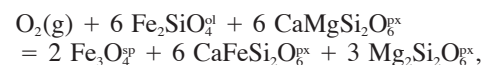
This procedure is essentially a general method for assigning a bulk composition to phase components, but as the masses involved represent small perturbations to an assemblage already near (metastable) equilibrium, the arbitrary nature of the assignment is not a disadvantage. Let j denote the phase to 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: $\delta\mathbf{m}_{sys} = \mathbf{T}_j\delta\mathbf{m}_j$, where the $nc \times na_j$ stoichiometry matrix $\mathbf{T}_j$ is a submatrix of $\mathbf{T}_{sys}$, 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_{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 $\delta\mathbf{m}_{sol}$ of perturbations to the number of moles of each phase in the assemblage. If $\mathbf{T}_{sol}$ is the $nc \times n_{sol}$ stoichiometry matrix that transforms the system components of the assemblage to the set of phase components we seek to modify ($\mathbf{T}_{sol} = \mathbf{T}_{sys}^T$), then the solution is expressed by the system of linear equations $\mathbf{T}_{sol}\delta\mathbf{m}_{sol} = \delta\mathbf{m}_{sys}$ that is, in general, underconstrained, i.e., there is an ($n_{sol} - nc$) dimensional space of solutions all of which satisfy the constraints. Solution of this system by SVD will produce the solution vector $\delta\mathbf{m}_{sol}$ that has the smallest 2-norm [i.e., the member of the solution family with minimum $(\delta\mathbf{m}_{sol}^T \cdot \delta\mathbf{m}_{sol})^{1/2}$]. 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 assemblage 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 $\mathbf{T}_{sol}$ as follows: let $\mathbf{m}_{sol}$ be the vector of total abundances of the n_{sol} phase components in the assemblage to be perturbed, and denote the $n_{sol} \times n_{sol}$ diagonal matrix with $\mathbf{m}_{sol}$ on the main diagonal as $\mathbf{M}_{sol}$. Since the matrix is diagonal, its inverse is simply the diagonal matrix with the reciprocal of each element of $\mathbf{m}_{sol}$ along its diagonal. Then we have $[\mathbf{T}_{sol} \cdot \mathbf{M}_{sol}] \cdot [\mathbf{M}_{sol}^{-1} \cdot \delta\mathbf{m}_{sol}] = \delta\mathbf{m}_{sys}$, which we solve using the SVD of $[\mathbf{T}_{sol} \cdot \mathbf{M}_{sol}]$. This yields on backsubstitution the particular solution $[\mathbf{M}_{sol}^{-1} \cdot \delta\mathbf{m}_{sol}]$ 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 $\mathbf{m}_{sol}$. The desired solution is then obtained simply by premultiplying the particular solution by $\mathbf{M}_{sol}$, which recovers the desired solution vector $\delta\mathbf{m}_{sol}$.

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_{O_2}

In order to perform calculations at constrained f_{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_{O_2} to the desired value before minimization (and to calculate f_{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 Fe_2O_3/FeO in silicate liquids as a function of composition, temperature, pressure, and f_{O_2}. In the absence of a liquid, a method is required that enforces the f_{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 Fe^{3+}- and 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:

$$O_2(g) + 6\ Fe_2SiO_4^{ol} + 6\ CaMgSi_2O_6^{px}$$
$$= 2\ Fe_3O_4^{sp} + 6\ CaFeSi_2O_6^{px} + 3\ Mg_2Si_2O_6^{px},$$

which can be expressed as

$$\sum_{i=1}^{6} n_i m_i = 0, \tag{3}$$

where $i = 1$ refers to 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

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

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

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

or more generally

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

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 $\delta\mathbf{m}_{sys}^*$ 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 $\delta\mathbf{m}_{sys}^{*\,T} = \{-1,0,0,0,0,2,-4,0,0,0\}$. Note that the first position in $\delta\mathbf{m}_{sys}^*$ 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 $\mathbf{T}_{sol}^*$, 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,

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

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

$$\sum_{i=1}^{m+1} n^*_{sol_i} m_i = 0 \qquad (8)$$

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 $\mathbf{M}_{sol}^*$ and assign a large value to the first element, representing $O_2(g)$. Then we compute the SVD of $[\mathbf{T}_{sol}^* \cdot \mathbf{M}_{sol}^*]$, back-substitute to obtain the weighted particular solution $[\mathbf{M}_{sol}^{*-1} \cdot \mathbf{n}_{sol}^*]$, and then recover the desired reaction stoichiometry $\mathbf{n}_{sol}^*$ by premultiplying by $\mathbf{M}_{sol}^*$. 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 $\mathbf{T}_{sol}^* = \mathbf{U} \cdot \text{diag}[\mathbf{w}] \cdot \mathbf{V}^T$ 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 SiO_2-TiO_2-Al_2O_3±Cr_2O_3-Fe_2O_3-FeO±NiO-MgO±MnO±CoO-CaO-Na_2O±K_2O, (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)	Fe_2SiO_4	forsterite (Fo)	Mg_2SiO_4
	monticellite (Mc)	$CaMgSiO_4$	tephroite (Tp)	Mn_2SiO_4
	Ni-olivine (NiOl)	Ni_2SiO_4	Co-olivine (CoOl)	Co_2SiO_4
pyroxene:	diopside (CDi, ODi)	$CaMgSi_2O_6$	essenite (CEs, OEs)	$CaFe^{3+}AlSiO_6$
	jadeite (CJd, OJd)	$NaAlSi_2O_6$	hedenbergite (CHd, OHd)	$CaFeSi_2O_6$
	enstatite (CEn, OEn)	$Mg_2Si_2O_6$	buffoonite (CBf, OBf)	$CaMg_{0.5}Ti_{0.5}Fe^{3+}SiO_6$
	aluminobuffoonite (CAbf, OAbf)	$CaMg_{0.5}Ti_{0.5}AlSiO_6$		
spinel:	hercynite (Hc)	$FeAl_2O_4$	chromite (Cr)	$FeCr_2O_4$
	spinel (Sp)	$MgAl_2O_4$	magnetite (Mt)	Fe_3O_4
	ulvospinel (Uv)	Fe_2TiO_4		
garnet:	pyrope (Py)	$Mg_3Al_2Si_3O_{12}$	almandine (Alm)	$Fe_3Al_2Si_3O_{12}$
	grossular (Gr)	$Ca_3Al_2Si_3O_{12}$		
feldspar:	albite (Ab)	$NaAlSi_3O_8$	anorthite (An)	$CaAl_2Si_2O_8$
	sanidine (Sd)	$KAlSi_3O_8$		

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 Cr_2O_3 is present spinel is mandatory and, if K_2O is included, feldspar in 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 (Cr_2O_3, MnO, NiO, CoO).
    Assign all Cr_2O_3 to Cr. Deduct Cr from FeO.
    Assign all MnO to Tp (Tp = 0.5 * MnO). Deduct Tp from SiO_2.
    Assign all NiO to NiOl (NiOl = 0.5 * NiO). Deduct NiOl from SiO_2.
    Assign all CoO to CoOl (CoOl = 0.5 * CoO). Deduct CoOl from SiO_2.

Rule 2 (Na_2O, K_2O). If the system contains K_2O, feldspar must be included.
    Assign all K_2O to Sd (Sd = 2*K_2O); deduct 0.5*Sd from Al_2O_3 and 3*Sd from SiO_2.
    If feldspar is to be included:
        Assign 0.9*Na_2O to Ab, leaving remainder for jadeite (Ab = 1.8*Na_2O); deduct 0.5*Ab from Al_2O_3 and 3*Ab from SiO_2.
        Assign 0.66*Na_2O to CJd (CJd = 1.32*Na_2O); deduct 0.5*CJd from Al_2O_3 and 2*CJd from SiO_2.
        Assign remaining Na_2O to OJd (OJd = 2.0*Na_2O); deduct 0.5*OJd from Al_2O_3 and 2*OJd from SiO_2.

Rule 3 (TiO_2, Fe_2O_3 in spinel).
    If spinel is to be included:
        Assign 0.25*TiO_2 to Uv; deduct 2*Uv from FeO.
        Assign 0.4*Fe_2O_3 to Mt; deduct Mt from FeO.

Rule 4 (Al_2O_3).
    If spinel is to be included:
        Assign 0.5*Al_2O_3 to Sp; deduct Sp from MgO.
        If (Mt + Cr + 2*Uv − 0.2*$Al2O_3$ > 0) assign −0.2*Al_2O_3 to Hc (i.e., set Hc = −0.2*Al_2O_3, and Al_2O_3 = 1.2*Al_2O_3) and add −Hc to FeO.
        else set Hc = (0.001 − Mt − Cr − 2*Uv), add −Hc to Al_2O_3 and FeO.
    If feldspar is to be included:
        Assign 0.64*Al_2O_3 to An; deduct An from CaO and 2*An from SiO_2.
    If garnet is to be included:
        Set temporary variable TotalGt = 0.6*Al_2O_3.
        Set Alm = TotalGt*[2.0*FeO/(2.0*FeO + 3.0*MgO + 0.5*CaO)]; deduct 2*Alm from FeO.
        Set Py = TotalGt*[3.0*MgO/(2.0*FeO + 3.0*MgO + 0.5*CaO)]; deduct 2*Py from MgO.
        Set Gr = TotalGt*[0.5*CaO/(2.0*FeO + 3.0*MgO + 0.5*CaO)]; deduct 2*Gr from CaO.
        Deduct TotalGt from Al_2O_3 and 3.0*TotalGt from SiO_2.

Rule 5 (TiO_2, Fe_2O_3, Al_2O_3). Perform all the following steps before deducting anything from TiO_2, Fe_2O_3, or Al_2O_3.
        Set OAbf = 0.75*(Al_2O_3 + TiO_2 − Fe_2O_3).
        Set CAbf = 0.25*(Al_2O_3 + TiO_2 − Fe_2O_3).
        Set OBf = 0.75*(Fe_2O_3 + TiO_2 − Al_2O_3).
        Set CBf = 0.25*(Fe_2O_3 + TiO_2 − Al_2O_3).
        Set OEs = 0.75*(Fe_2O_3 + Al_2O_3 − TiO_2).
        Set CEs = 0.25*(Fe_2O_3 + Al_2O_3 − TiO_2).
        Deduct (Al_2O_3 + TiO_2 + Fe_2O_3) from CaO and SiO_2.
        Deduct TiO_2 from MgO.
        Set TiO_2, Fe_2O_3, and Al_2O_3 equal to zero.

Rule 6 (CaO). Perform the following steps before modifying CaO:
        Set CHd = 0.15*CaO. Deduct CHd from FeO and 2*CHd from SiO_2.
        If olivine is to be (provisionally) included, set OHd = CaO, else set OHd = FeO.
        Set ODi = −1.05*OHd.
    Deduct (CHd + OHd + ODi) from CaO.
    Deduct ODi from MgO. Deduct OHd from FeO.
    Deduct 2*(OHd + ODi) from SiO_2.
    If olivine is to be (provisionally) included, set CDi = 0.833*CaO, else set CDi = CaO.
    Deduct CDi from CaO and MgO. Deduct 2*CDi from SiO_2.
    If (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 SiO_2.

Rule 7 (MgO, FeO, SiO_2).
    If olivine is to be included assign remaining FeO to Fa (Fa = 0.5*FeO); deduct Fa from SiO_2.
    If (MgO > SiO_2) and olivine is to be included, set Fo = (MgO − SiO_2); deduct Fo from SiO_2 and 2*Fo from MgO.
    Set OEn = 0.475*MgO; deduct 2*OEn from MgO and SiO_2.
    Assign remaining MgO to CEn (CEn = 0.5*MgO). Deduct 2*CEn from SiO_2.
    If (SiO_2 > 0), a silica excess exists. Add quartz to the assemblage and assign all remaining SiO_2 to quartz.
    If any oxide is not now equal to zero, the composition is infeasible. End in defeat, or else return successfully.