

An order-disorder model for omphacitic pyroxenes in the system jadeite-diopside-hedenbergite-acmite, with applications to eclogitic rocks

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ABSTRACT

A new thermodynamic model for sodic pyroxenes involving jadeite-diopside-hedenbergite-acmite is presented. This model allows for ordering of Mg, Al, Fe²⁺, and Fe³⁺ on the M1 sites, with coupled Na and Ca ordering on the M2 sites. It is calibrated on the basis of experiments in three chemical subsystems together with available information on ordering in different pyroxenes and on the limited calorimetric data. Central to the determination of the parameters of the model is the use of relationships among the end-member Gibbs energies and the interaction energies in the various possible non-independent sets of end-members. An important aspect of this model, which uses the symmetric formalism, is that Fe-Mg (FM) and Al-Fe³⁺ (AF') mixing is not assumed to be ideal. The model accounts successfully for the experiments at both 600 °C and at higher temperatures involving ordered and disordered pyroxenes coexisting with albite and quartz in NCMAS, NCFAS, NF'AS systems as well as the available calorimetry. It is also able to predict the positions and slopes of tielines in coexisting jadeite + omphacite and omphacite + augite found in nature at lower temperatures. Although the model requires a large number of energy parameters, some of these are not critical to the behavior of the model, while for others the constraints from experiment, calorimetry, ordering state and solvi lead to very limited allowable combinations. The model places some restrictive constraints on the shape of the phase relations in the jadeite-augite-acmite system. Petrological applications of the model are illustrated via a phase diagram example for a MORB bulk composition eclogite.

Keywords: Thermodynamics, omphacite, activity-model, eclogite, phase equilibria, metamorphic petrology, mixing properties

INTRODUCTION

Omphacite is the name given to ordered (space group *P2/n*) pyroxenes at intermediate compositions along the Na(Al,Fe³⁺)Si₂O₆-Ca(Mg,Fe)Si₂O₆ join. Disordered high-temperature clinopyroxenes have space group *C2/c*. Focusing on the join NaAlSi₂O₆-Ca(Mg,Fe)Si₂O₆, the onset of ordering below $T_c \approx 860$ °C (Carpenter 1981) is driven by partitioning of Mg and Al onto separate M1m and M1a sites, which are equivalent above the critical temperature. The M2 sites also split into Na-preferring M2n and Ca-preferring M2c sites below T_c . The thermodynamics of omphacite ordering have been investigated in terms of generalized Bragg-Williams models (Davidson and Burton 1987), by Landau theory (Carpenter et al. 1990; Holland 1990), by symmetric formalism (Holland and Powell 1996b) and, more recently, by cluster variation models (Vinograd 2002a, 2002b). Neither the Landau theory, which uses only a non-configurational entropy, nor the models of Vinograd (2002a, 2002b) can be readily formulated for dealing with complex solid solutions

with several order parameters, and so the simpler symmetric formalism (Holland and Powell 1996a, 1996b) will be used in this study. Although the symmetric formalism does not handle short-range order explicitly, the energetic effects of short-range order closely follow those of long-range order (Holland and Powell 1998), and the field term, introducing non-convergent ordering, may be used to simulate the effects of short-range order above any transformation temperature (Holland and Powell 1996a). Because of the charge-balanced substitution CaMg-NaAl, the ordering on M2 is not independent of that on M1. This simple assumption is corroborated by: (1) the finding of Carpenter et al. (1990) that the order parameter on M2 is linearly dependent on that for M1; and (2) that for convergent omphacite both individual order parameters must go to zero at T_c .

Omphacitic clinopyroxenes occur commonly in metabasic rocks at high and ultrahigh pressures. These pyroxenes, with garnet, play a pivotal role in determining conditions of formation of eclogites, as well as in general being essential in mineral equilibria modeling at such conditions. Although the omphacite model of Holland and Powell (1996b) has been used successfully for modeling rock phase equilibria in Na₂O-CaO-K₂O-FeO-MgO-Al₂O₃-SiO₂-H₂O (e.g., Wei et al. 2003), that model used

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equipartition, a device for distributing Fe^{2+} and Mg between the sites on which they occur in proportion to the mineral's bulk $\text{Fe}^{2+}:\text{Mg}$ ratio. However equipartition is now discredited (Holland and Powell 2006), requiring that the model be reworked. Moreover, with the key role of ferric iron in phase equilibria modeling, including garnet-clinopyroxene thermometry (e.g., Stipska and Powell 2005), a new model for omphacite is needed in $\text{Na}_2\text{O}-\text{CaO}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$ (NCFMAF'S). This paper aims to provide one.

MODELING OMPHACITE IN NCMAS

Consider the end-members, diopside (di), jadeite (jd), and the ordered end-member om. In such omphacites, Al and Mg may order on the M1 sites, and Ca and Na may order on the M2 sites. As stated earlier we shall assume that the ordering state in M2 and M1 sites is identical, allowing a single parameter Q to monitor the ordering. The composition and order parameters may be defined as follows:

$$X = \frac{1}{2}(X_{\text{Na}}^{\text{M2c}} + X_{\text{Na}}^{\text{M2n}})$$

$$Q = \frac{1}{2}(X_{\text{Al}}^{\text{M1a}} - X_{\text{Al}}^{\text{M1m}}) = \frac{1}{2}(X_{\text{Na}}^{\text{M2n}} - X_{\text{Na}}^{\text{M2c}})$$
(1)

where X is the jadeite mole fraction and Q is the order parameter. The site fractions in the partially ordered pyroxene become

$$\begin{aligned} x_{\text{Mg}}^{\text{M1m}} &= 1 - X + Q \\ x_{\text{Al}}^{\text{M1m}} &= X - Q \\ x_{\text{Mg}}^{\text{M1a}} &= 1 - X - Q \\ x_{\text{Al}}^{\text{M1a}} &= X + Q \\ x_{\text{Na}}^{\text{M2c}} &= X - Q \\ x_{\text{Ca}}^{\text{M2c}} &= 1 - X + Q \\ x_{\text{Na}}^{\text{M2n}} &= X + Q \\ x_{\text{Ca}}^{\text{M2n}} &= 1 - X - Q \end{aligned}$$
(2)

and the proportions of the end-members are given by

$$\begin{aligned} p_{\text{jd}} &= X - Q \\ p_{\text{di}} &= 1 - X - Q \\ p_{\text{om}} &= 2Q \end{aligned}$$
(3)

The state of order can vary from complete disorder, $Q = 0$, to complete order, $Q = 2X$ for $X \leq 0.5$, and $Q = 2(1 - X)$ for $X \geq 0.5$. The equilibrium state of order as a function of composition and temperature in the di-jd-om system is given by the (internal) equilibrium relationship for the reaction between the end-members (Holland and Powell 1996b), $\text{di} + \text{jd} = 2 \text{om}$:

$$0 = A + BQ + CX + RT \ln K_D$$
(4)

in which:

$$\begin{aligned} A &= \Delta H_{\text{R}}^{\text{om}} - W_{\text{dijd}} + 2W_{\text{diom}} \\ B &= W_{\text{dijd}} - 2(W_{\text{diom}} + W_{\text{jdom}}) \\ C &= 2(W_{\text{jdom}} - W_{\text{diom}}) \\ K_D &= \frac{(a_{\text{om}}^{\text{ideal}})^2}{(a_{\text{jd}}^{\text{ideal}})(a_{\text{di}}^{\text{ideal}})} \end{aligned}$$
(5)

In these expressions $\Delta H_{\text{R}}^{\text{om}}$ is the enthalpy of the ordering reaction $\text{jd} + \text{di} = 2 \text{om}$, the W_{ij} are the interaction energies for the ij end-member pairs, and K_D is the equilibrium constant for the ordering reaction written in terms of the ideal activities. Assuming that omphacite disorders convergently (Carpenter 1981), at $T_c = 860 \pm 30$ °C, we have the pair of conditions for $X = 0.5$

$$\begin{aligned} B &= -4RT_c = W_{\text{dijd}} - 2(W_{\text{diom}} + W_{\text{jdom}}) \\ 0 &= A + \frac{C}{2} = \Delta H_{\text{R}}^{\text{om}} - W_{\text{dijd}} + (W_{\text{diom}} + W_{\text{jdom}}) \end{aligned}$$
(6)

These two conditions, coupled with the experiments on compositions of pyroxenes at 600 °C of Holland (1983) impose very restrictive constraints on the parameters. First, a value for $W_{\text{dijd}} = 26.0 \pm 1.0$ kJ was determined by Holland (1983) from modeling the experiments on the disordered, diopside-rich, pyroxenes coexisting with albite and quartz. Second, the first condition above implies that $W_{\text{diom}} + W_{\text{jdom}}$ must sum to $(4RT_c + W_{\text{dijd}})/2$. Fixing a value for W_{diom} therefore determines the value for W_{jdom} . Trial and error fitting of the experiments of Holland (1983) shows that only a value of W_{diom} of 15.75 ± 0.25 gives the experimental width of the diopside-omphacite miscibility gap at 600 °C. A good fit to the P - X_{jd} data of Holland (1983) yields the following parameters:

$$\begin{aligned} W_{\text{dijd}} &= 26.0 \pm 1.0 \text{ kJ} \\ W_{\text{diom}} &= 15.75 \pm 0.3 \text{ kJ} \\ W_{\text{jdom}} &= 15.5 \pm 0.7 \text{ kJ} \\ \Delta H_{\text{R}}^{\text{om}} &= -5.6 \pm 0.4 \text{ kJ} \end{aligned}$$
(7)

These values differ a little from those proposed in the exploratory work reported in Holland and Powell (1996b) in that the system has been allowed to be very slightly nonconvergent (by adoption of a small field term, $A + C/2$) and slightly asymmetric (by making W_{diom} slightly larger than W_{jdom}) to fit the experiments of Holland (1983) better. This small nonconvergent character leads to disordering at around 850 °C, with a field term of -0.35 kJ preventing the order parameter going to zero there. All attempts to enforce a larger miscibility gap on the jadeite-rich side (as postulated by Carpenter 1983) cause poor fits to the experimental data and violate the constraints discussed above, while attempts to reduce the width of the miscibility gap on the diopside-rich side cause the omphacite to become highly non-convergent.

The behavior of order parameter Q with temperature is shown in Figure 1, where the small field term leads to a slightly non-convergent ordering. This system shows development of paired miscibility gaps at low temperature, with dashed near-critical curves connecting them (Fig. 2). There is no phase transition across this curve, simply a rapid decrease in order.

We note, in passing, that attempts were made to introduce asymmetry into the energetics by using a modified Van Laar approach (the asymmetric formalism, Holland and Powell 2003). This provided no additional gains, as the system appears to be quite symmetric anyway ($W_{\text{diom}} \approx W_{\text{jdom}}$), and enough asymmetry can be introduced by making $W_{\text{diom}} \geq W_{\text{jdom}}$. The uncertainties on all parameters in this study are estimated without regard for correlations, and should be treated as approximate.

MODELING OMPHACITE IN NCFMAS

Ferro-omphacites in NCFAS

Substitution of Fe for Mg yields a system jadeite-ferro-omphacite-hedenbergite (jd-fom-hed), analogous to the jd-om-di system described above. To determine the parameters of this ferrous subsystem, we make some simple assumptions and use the compositions of coexisting pyroxenes with albite and quartz from the experiments of Aranovich and Perchuk (1989). Specifically we assume initially: (1) that the ordering is nearly convergent; (2) the magnitude of $W_{\text{jdhed}} = 24 \pm 2$ kJ from the experiments of Aranovich and Perchuk, as analyzed by Holland (1990); and (3) that the ordering enthalpy for the reaction $\text{hed} + \text{jd} = 2 \text{ fom}$ is similar to that for Mg-omphacite, at around -6 kJ. These assumptions imply that the sum $W_{\text{jd fom}} + W_{\text{hed fom}} \approx 29$ kJ and that $T_c \approx 750$ °C. Individual values for the interaction energies may be refined from these initial estimates on the basis of observed tie lines between coexisting omphacite and augite in nature (Tsujiyori 2005) as discussed further in the next section, leading to the parameter set:

$$\begin{aligned} W_{\text{jdhed}} &= 24.0 \pm 2 \text{ kJ} \\ W_{\text{jd fom}} &= 14.0 \pm 1.5 \text{ kJ} \\ W_{\text{hed fom}} &= 14.5 \pm 1.5 \text{ kJ} \\ \Delta H_{\text{R}}^{\text{om}} &= -7.2 \pm 2 \text{ kJ} \end{aligned} \quad (8)$$

The order parameter variation with temperature is less convergent than for Mg-omphacite (Fig. 1) and the binary jd-hed diagram looks analogous to the jd-di diagram, but with a lower critical temperature, and solvi that close at lower temperature (Fig. 2). This result is very reasonable, given that the W values are proportionally lower than in the corresponding jd-di system; if we assume, as in Dale et al. (2005), that the parameters in the Fe subsystem are simply proportional to those in the Mg subsystem, then the values for $W_{\text{jd fom}}$ and $W_{\text{hed fom}}$ become 14.3 and 14.5 kJ/mol, very similar to those optimized here. These values also make sense by analogy with other iron-bearing systems (e.g., the miscibility gap between hedenbergite and ferrosilite is lower than that between diopside and enstatite, and the melting temperatures of Fe-silicates are lower than the corresponding Mg-silicate equivalents).

Ferromagnesian omphacites in NCFMAS

The introduction of ferrous iron into the system complicates matters in that Fe and Mg may partition unequally among the available sites, as is known to occur in Fe-Mg orthopyroxenes and calcic clinopyroxenes (e.g., Carpenter and Salje 1994; Yang and Ghose 1994).

The compositions of the five end-members needed to describe omphacites in the system NCFMAS are given below in terms of site occupancies of the subdivided M1 and M2 sites. Calcium and Na are ordered over M2c and M2n, while Mg, Fe, and Al are ordered on M1m and M1a sites. For a pyroxene formula based upon 6 O atoms ($\text{NaAlSi}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$) the site distributions are as follows:

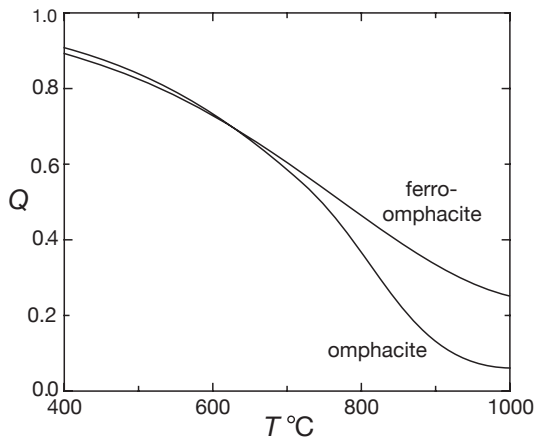
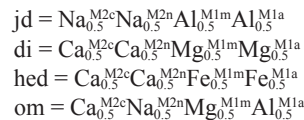


FIGURE 1. Variation of order parameter Q with temperature for omphacite and ferro-omphacite using the parameters described in the text.

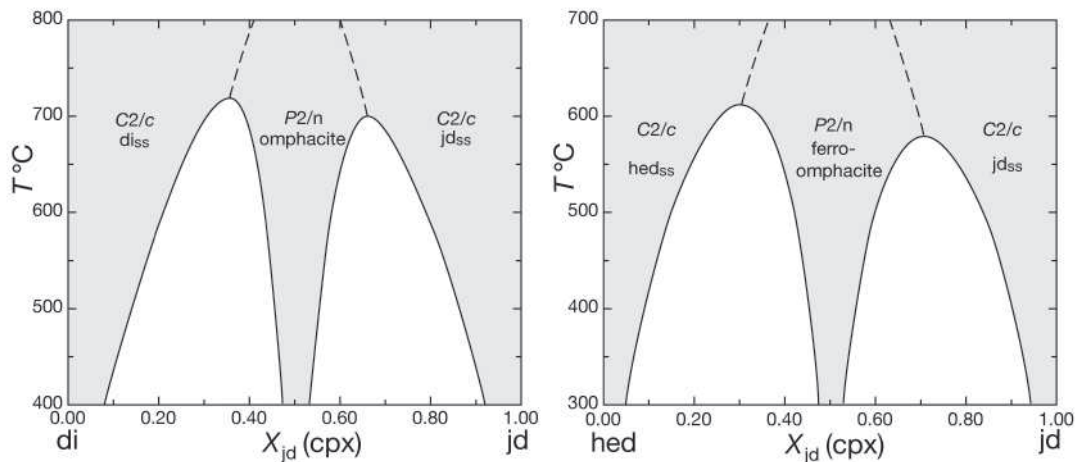
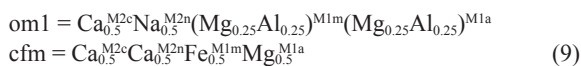


FIGURE 2. The diopside-jadeite and hedenbergite-jadeite phase diagrams calculated using the parameters from this study. Note that the temperature scales on the two T - X diagrams are different.



Here the end-members used are jadeite (jd), diopside (di), hedenbergite (hed), ordered omphacite (om), M2-ordered omphacite (om1), and an ordered Ca-Fe-Mg end-member (cfm). If the variables used to describe compositional and ordering state are as follows below, with x being the Fe:(Fe + Mg) ratio, j the jadeite content, Q_1 and Q_2 the order parameters for Mg:Al and Na:Ca ordering on the M1 and M2 sites, respectively, and Q_{fm} the Fe:Mg order parameter for M1:

$$\begin{aligned} x &= (x_{\text{Fe}}^{\text{M1m}} + x_{\text{Fe}}^{\text{M1a}})/(x_{\text{Fe}}^{\text{M1m}} + x_{\text{Fe}}^{\text{M1a}} + x_{\text{Mg}}^{\text{M1m}} + x_{\text{Mg}}^{\text{M1a}}) \\ j &= (x_{\text{Na}}^{\text{M2c}} + x_{\text{Na}}^{\text{M2n}})/2 \\ Q_1 &= (x_{\text{Al}}^{\text{M1a}} - x_{\text{Al}}^{\text{M1m}})/2 \\ Q_2 &= (x_{\text{Na}}^{\text{M2n}} - x_{\text{Na}}^{\text{M2c}})/2 \\ Q_{\text{fm}} &= x_{\text{Fe}}^{\text{M1m}}/(x_{\text{Fe}}^{\text{M1m}} + x_{\text{Mg}}^{\text{M1m}}) - x \end{aligned} \quad (10)$$

To simplify matters, the state of order on the M1 and M2 sites will be set to be the same. This reduces the number of order parameters by one ($Q = Q_2 = Q_1$) and eliminates the need for the om1 end-member. Then the site fractions become:

$$\begin{aligned} x_{\text{Mg}}^{\text{M1m}} &= 1 - j + Q + x(j - Q - 1) + Q_{\text{fm}}(j - Q - 1) \\ x_{\text{Fe}}^{\text{M1m}} &= x(1 - j + Q) + Q_{\text{fm}}(1 - j + Q) \\ x_{\text{Al}}^{\text{M1m}} &= j - Q \\ x_{\text{Mg}}^{\text{M1a}} &= 1 - j - Q + x(j + Q - 1) + Q_{\text{fm}}(1 - j + Q) \\ x_{\text{Fe}}^{\text{M1a}} &= x(1 - j - Q) + Q_{\text{fm}}(j - Q - 1) \\ x_{\text{Al}}^{\text{M1a}} &= j + Q \\ x_{\text{Na}}^{\text{M2c}} &= j - Q \\ x_{\text{Ca}}^{\text{M2c}} &= 1 - j + Q \\ x_{\text{Na}}^{\text{M2n}} &= j + Q \\ x_{\text{Ca}}^{\text{M2n}} &= 1 - j - Q \end{aligned} \quad (11)$$

and the proportions of the end-members become:

$$\begin{aligned} p_{\text{jd}} &= j - Q \\ p_{\text{di}} &= 1 - j - Q + x(j - Q - 1) + Q_{\text{fm}}(j - Q - 1) \\ p_{\text{hed}} &= x(1 - j - Q) + Q_{\text{fm}}(j - Q - 1) \\ p_{\text{om}} &= 2Q \\ p_{\text{cfm}} &= 2Qx + 2Q_{\text{fm}}(1 - j + Q) \end{aligned} \quad (12)$$

The thermodynamic model involves writing the ideal activities of the end-members using the standard mixing-on-sites approach, coupled with the symmetric formalism for the non-ideal contributions as in Powell and Holland (1993). Details are provided in the appendix.

Energetics of mixing in NCFMAS

The model described above comprises an independent set of five end-members (jd, di, om, hed, cfm). Interaction energies among these end-members are required that satisfy the known properties of omphacites in terms of order-disorder and mixing behavior. The values derived here are summarized in Table 1 and their derivation is described below.

First, the parameters involving di-hed-cfm determine the Fe-Mg partitioning on the M1 site. This is likely to be of minor importance as the site is a regular octahedron (M1) like in oliv-

ines, and so partitioning is expected to be minimal. The order-disorder relations among the Na-free clinopyroxenes along the di-hed join are assumed to behave similarly to orthopyroxenes in that the energetics will be governed by non-convergent ordering with individual Fe-Mg interactions of around 4 kJ/mol per site (Holland and Powell 2006). Thus W_{hedcfm} and W_{dicfm} are set to 2 ± 1 kJ/mol, and the value for W_{dihed} is set to 4 ± 1 kJ/mol because the number of atoms of Fe and Mg mixing in the di-hed binary is double that of the hed-cfm and di-cfm binaries.

The interactions among jd, di, and om have been already discussed above. Although the fom end-member is not part of the independent set, values for interaction energies involving fom-jd-hed and, particularly, $\Delta H_{\text{R}}^{\text{fom}}$ do provide important constraints on the interaction energies among the five end-members in the chosen set. With fom involved, there are six end-members and hence $n(n-1)/2 = 15$ interaction energies, but, for the independent set of five end-members involving 10 interaction energies, there will be 5 W equivalences and one enthalpy relation (Powell and Holland 1999), which help impose restrictions on the values of the remaining unknown terms:

$$\begin{aligned} W_{\text{cfmfom}} &= W_{\text{diom}} \\ W_{\text{difom}} &= 2W_{\text{dicfm}} + 2W_{\text{diom}} - W_{\text{omcfm}} \\ W_{\text{hedfom}} &= W_{\text{dicfm}} - W_{\text{dihed}} + W_{\text{diom}} + W_{\text{hedcfm}} + W_{\text{hedom}} - W_{\text{omcfm}} \\ W_{\text{jdfom}} &= W_{\text{dicfm}} + W_{\text{diom}} + W_{\text{jdcfm}} - W_{\text{jddi}} + W_{\text{jdom}} - W_{\text{omcfm}} \\ W_{\text{omfom}} &= W_{\text{dicfm}} \\ H_{\text{fom}} &= H_{\text{cfm}} - H_{\text{di}} + H_{\text{om}} - W_{\text{dicfm}} - W_{\text{diom}} + W_{\text{omcfm}} \end{aligned} \quad (13)$$

The following parameters are assumed known from the discussion above:

$$\begin{aligned} W_{\text{jddi}} &= 26 \pm 1 \text{ kJ} \\ W_{\text{diom}} &= 15.75 \pm 0.3 \text{ kJ} \\ W_{\text{jdom}} &= 15.5 \pm 0.7 \text{ kJ} \\ W_{\text{dihed}} &= 4 \pm 1 \text{ kJ} \\ W_{\text{dicfm}} &= 2 \pm 1 \text{ kJ} \\ W_{\text{hedcfm}} &= 2 \pm 1 \text{ kJ} \\ W_{\text{hedfom}} + W_{\text{jdfom}} &\approx 29 \text{ kJ} \\ \Delta H_{\text{om}} &= -5.6 \pm 0.4 \text{ kJ} \\ \Delta H_{\text{cfm}} &= -3.0 \pm 1 \text{ kJ} \end{aligned} \quad (14)$$

There is insufficient information to determine all remaining parameters from the 6 equivalence relations above, but they can all be described relative to an assumed value for $y = -(\Delta H_{\text{R}}^{\text{fom}})/2$, and the magnitudes for W_{hedfom} and W_{jdfom} that leads to,

$$\begin{aligned} W_{\text{cfmfom}} &= 15.75 \text{ kJ} \\ W_{\text{difom}} &= 13.45 + y \text{ kJ} \\ W_{\text{hedom}} &= W_{\text{hedom}} + 6.3 - y \text{ kJ} \\ W_{\text{jdcfm}} &= W_{\text{jdfom}} + 14.8 - y \text{ kJ} \\ W_{\text{omfom}} &= 2 \text{ kJ} \\ W_{\text{omcfm}} &= 22.05 - y \text{ kJ} \end{aligned} \quad (15)$$

Setting y leaves only the two parameters W_{hedfom} and W_{jdfom} to be found, subject to their sum being constrained. Tie lines between coexisting omphacite and augite observed in natural pyroxenes (Tsujiyori 2005) show that the omphacites are more Fe-rich than the augites, and the correct partitioning can be

achieved by setting $W_{\text{hedfom}} = 14.5 \pm 1$ kJ/mol and $W_{\text{jdfom}} = 14 \pm 1$ kJ/mol and a value for $\gamma = 3.6 \pm 1$ kJ/mol. Making γ smaller than this makes fom disorder more convergently (like om) but causes the tie lines to rotate such that the natural data are not satisfied. The calculated diagram for coexisting jadeites, omphacites, and augites in the system NCFMAS is illustrated in Figure 3 where the calculated tie lines are shown along with two natural sets of mineral pairs. The agreement appears satisfactory, any small discrepancies probably occurring because the natural pairs contain ferric iron and were formed at such low temperatures (350 °C according to Tsujimori 2005) that equilibrium might not have been obtained.

ADDITION OF FERRIC IRON—ACMITIC OMPHACITES

Addition of Fe^{3+} to the system introduces the acmite end-member $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ into the model. An added complication, about which very little is known, is the possibility that Fe^{3+} and Al may order on the M1a and M1m sites. On addition of Fe^{3+} to this model, a further order parameter Q_{af} and ordered end-member jac ($\text{NaAl}_{0.5}\text{Fe}_{0.5}^{3+}\text{Si}_2\text{O}_6$) are required. Although one simplification might be to assume that all Fe-Al interactions are ideal and that $\Delta H_{\text{R}}^{\text{jac}} = 0$, the experimental work of Liu and Bohlen (1995) on coexisting jadeite-acmite solid solutions with albite and quartz do allow for a small amount of non-ideality, and a good fit to their experimental data (Fig. 4) yields the following parameters for the jd-jac-acm system, in which a small positive interaction energy is offset by the slight ordering enthalpy:

$$\begin{aligned} W_{\text{jdacm}} &= 5 \pm 2 \text{ kJ} \\ W_{\text{jdjac}} &= 3 \pm 1 \text{ kJ} \\ W_{\text{acmjac}} &= 3 \pm 1 \text{ kJ} \\ \Delta H_{\text{R}}^{\text{jac}} &= -2.0 \pm 2 \text{ kJ} \end{aligned} \quad (16)$$

Adding Mg to this simple jadeite-acmite binary to make the ternary jadeite-acmite-diopside provides a useful first compari-

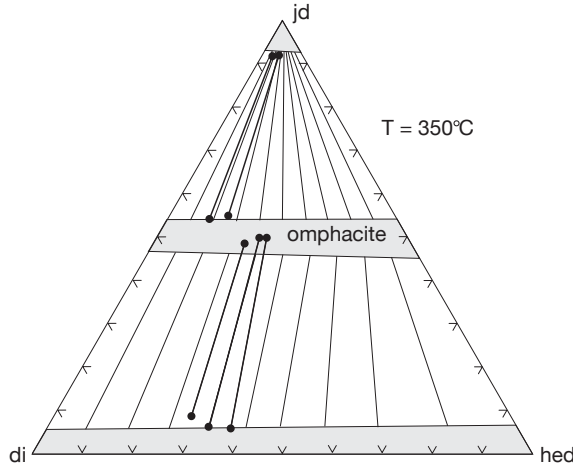


FIGURE 3. The calculated diopside-hedenbergite-jadeite phase diagram at 350 °C, showing the ordered omphacite region and coexisting disordered jadeite and diopside solid solutions. Natural data from Tsujimori et al. (1997) and Tsujimori (2005) are shown for comparison. Natural jadeites contain significant ferric iron, and are represented in the diagram by substituting an equivalent amount of Al for comparison to model calculations.

son with natural omphacites, and some debate has centered on the disposition of miscibility gaps between jadeite, omphacite, augite, and acmitic pyroxenes (e.g., Matsumoto and Hirajima 2005). The parameters needed for a model in this subsystem, as deduced below, are displayed in Table 2.

There are four new parameters to find (W_{diacm} , W_{djac} , W_{omacm} , and W_{omjac}) before this system can be determined. To do this means using parameters already determined above, coupled with estimates from the system diopside-acmite (and the dependent intermediate ordered dac end-member $\text{Na}_{0.5}\text{Ca}_{0.5}\text{Fe}_{0.5}^{3+}\text{Mg}_{1/2}\text{Si}_2\text{O}_6$). It is likely that ordering between diopside and acmite is less pronounced than between jadeite and diopside because natural compositions half way between the augite and acmite end-members are much less ordered (Carpenter 1979), and so we will assume that the interaction energies W_{didac} and W_{acmdac} are only 10 ± 3 kJ/mol and that the ordering enthalpy ($\Delta H_{\text{R}}^{\text{jac}} = -6 \pm 2$ kJ/mol) is similar to that for omphacite. With a value for $W_{\text{acmdi}} = 15 \pm 3$ kJ/mol this leads to a disordering temperature of around 480 °C. The relationships among dependent end-members (Powell and Holland 1999) then allow all the parameters to be determined in this subsystem. These values are estimates only, and were varied somewhat to see what effect they might have on the calculated phase relations in the ternary di-jd-acm diagram. The diagram calculated for 500 °C is shown in Figure 5, in which the main features to be seen are the pair of miscibility gaps on either side of the omphacite composition that extend some way into the ternary toward acmite. The ordered region extends all the way to the dac composition, the dashed lines marking the locus of the

TABLE 1. Model interaction energies for the jd-di-hed system

W_{ij}	di	om	hed	cfm	
jd	26 ± 1	15.5 ± 0.7	24 ± 2	25.2 ± 2.5	kJ
di		15.75 ± 0.3	4 ± 1	2 ± 1	kJ
om			17.2 ± 2.5	18.45 ± 2	kJ
hed				2 ± 1	kJ

TABLE 2. Model interaction energies for the jd-di-acm system

	di	om	acm	jac	
jd	26 ± 1	15.5 ± 0.7	5 ± 1	3 ± 1	kJ
di		15.75 ± 0.3	15 ± 2	21.05 ± 3	kJ
om			12.8 ± 3	19.3 ± 3	kJ
acm				3 ± 1	kJ

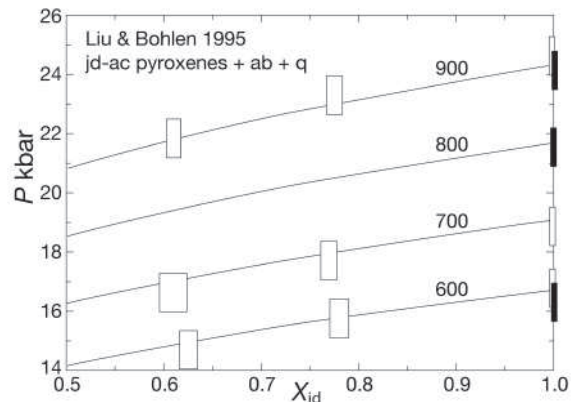


FIGURE 4. Experimental data together with calculated curves (for 600–900 °C) for compositions of jadeite-acmite pyroxenes coexisting with albite and quartz using the model of this study. Open symbols = Liu and Bohlen (1995); black symbols = Holland (1980).

order parameter at $Q = 0.15$ level. This diagram is in remarkably good agreement with the predictions of Carpenter (1983), and Matsumoto and Hirajima (2005) based on natural occurrences, particularly when the effects of Fe^{2+} are factored in (miscibility gaps would be smaller and the intermediate compositions between augite and acmite would be less ordered).

Addition of hedenbergite leads to the full omphacite model in the system NCFMF'AS. The parameters required in the full model are given in Table 3.

As discussed above, the extra terms were determined by combining estimates for ordering in the system hed-acm (with an ordered intermediate hac end-member) with the dependent end-member relationships. The hed-acm system is assumed to be similar to the di-acm system but with slightly smaller interaction energies. The following interaction energies are assumed known from the systems di-jd-hed and jd-acm-di (see above): W_{didac} , W_{acmdi} , W_{acmdac} , W_{dihed} , W_{dicfm} , W_{hedcfm} , W_{daccfm} . The values for $W_{\text{hedacm}} = 12 \pm 2$ kJ, $W_{\text{hedhac}} = 9 \pm 2$ kJ, and $W_{\text{acmhac}} = 9 \pm 2$ kJ were assumed to be similar to but a little smaller than the equivalent pairs in the di-acm-dac system, because in the omphacite system the parameters for the Fe subsystem (jd-hed-fom) are smaller than those in the Mg subsystem (jd-di-om). The remaining parameters may be found by substituting the known values above in the dependent end-member relationships (Powell and Holland 1999) below:

$$\begin{aligned} H_{\text{hac}} &= H_{\text{cfm}} + H_{\text{dac}} - H_{\text{di}} + W_{\text{daccfm}} - W_{\text{dicfm}} - W_{\text{didac}} \\ W_{\text{acmhac}} &= W_{\text{acmcfm}} + W_{\text{acmdac}} - W_{\text{acmdi}} - W_{\text{daccfm}} + W_{\text{dicfm}} + W_{\text{didac}} \\ W_{\text{cfmhac}} &= W_{\text{didac}} \\ W_{\text{dachac}} &= W_{\text{dicfm}} \end{aligned}$$

TABLE 3. Model interaction energies for the full jd-di-hed-acm system

	di	om	hed	cfm	acm	jac	
jd	26 ± 1	15.5 ± 0.7	24 ± 2	25.2 ± 2.5	5 ± 2	3 ± 1	kJ
di		15.75 ± 0.3	4 ± 1	2 ± 1	15 ± 2	21.05 ± 3	kJ
om			17.2 ± 2.5	18.45 ± 2	12.8 ± 3	19.3 ± 3	kJ
hed				2 ± 1	14 ± 1	20.1 ± 3.5	kJ
cfm					15.5 ± 4	21.05 ± 3	kJ
acm						3 ± 1	kJ

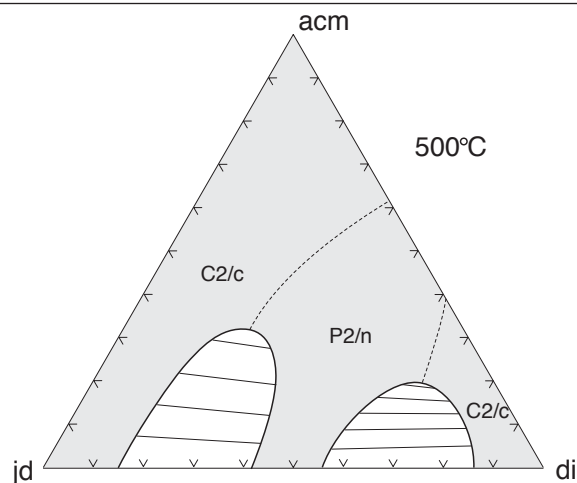


FIGURE 5. The calculated jadeite-diopside-acmite phase diagram at 500 °C, showing the ordered ($P2/n$) omphacite region and miscibility gaps with coexisting disordered ($C2/c$) jadeite and diopside solid solutions.

$$\begin{aligned} W_{\text{dihac}} &= W_{\text{daccfm}} + 2(W_{\text{dicfm}} + W_{\text{didac}}) \\ W_{\text{hedhac}} &= -W_{\text{daccfm}} + W_{\text{dicfm}} + W_{\text{didac}} - W_{\text{dihed}} + W_{\text{hedcfm}} + W_{\text{heddac}} \end{aligned} \quad (17)$$

together with the ordering reactions (given earlier in the text):

$$\begin{aligned} H_{\text{cfm}} &= \frac{1}{2}H_{\text{di}} + \frac{1}{2}H_{\text{hed}} - 1.5 \\ H_{\text{dac}} &= \frac{1}{2}H_{\text{di}} + \frac{1}{2}H_{\text{acm}} - 3.0 \end{aligned} \quad (18)$$

which leads to the enthalpy of the hac end-member

$$H_{\text{hac}} = \frac{1}{2}H_{\text{acm}} + \frac{1}{2}H_{\text{hed}} - 3.0 \text{ kJ} \quad (19)$$

and remaining mixing parameters for this subsystem:

$$\begin{aligned} W_{\text{acmcfm}} &= 15.5 \pm 4 \text{ kJ} \\ W_{\text{cfmhac}} &= 10.0 \pm 2 \text{ kJ} \\ W_{\text{dihac}} &= 10.5 \pm 1 \text{ kJ} \\ W_{\text{heddac}} &= 12.5 \pm 4 \text{ kJ} \end{aligned} \quad (20)$$

Many of the assumptions above are reasonable, but will require testing and perhaps future refinement.

DISCUSSION AND APPLICATIONS

The omphacite model presented here is the first solid solution, to our knowledge, to be modeled with three order parameters for petrological calculations. An obvious application of the new model is to MORB bulk compositions at conditions of eclogite facies metamorphism close to 20 kbar and 600 °C, giving rise to so-called “hydrous” eclogites, typical of orogenic belts such as the Alps (e.g., Holland 1979; Davis and Whitney 2006).

The MORB composition used is that of Sun and McDonough (1989), which includes analyzed ferric iron. Such a composition can therefore be modeled in $\text{Na}_2\text{O}-\text{CaO}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{TiO}_2-\text{O}$ (NCFMASHTO), the “O” representing ferric iron. However, initially the composition is modeled with a pressure-temperature pseudosection in NCFMASH, ignoring titanium and ferric iron, to show the phase relations in this limiting reduced state (Fig. 6). A pressure-temperature pseudosection for the complete bulk composition in NCFMASHTO, using particularly the analyzed ferric iron, is presented in Figure 7. Whereas the NCFMASH diagram is unlikely to be applicable to rocks, a range of oxidation state either side of that represented by the Sun and McDonough composition is likely to be observed in rocks. For example sulfide-bearing rocks may be more reduced and sea-floor altered rocks may be more oxidized than the Sun and McDonough composition.

The pseudosection in Figure 6 shows the NCFMASH phase relations at these conditions involving garnet + omphacite + quartz with various combinations of the phases lawsonite, glaucophane, calcic amphibole, clinozoisite, talc, and kyanite. The calcic amphibole (“actinolite”: see Dale et al. 2005 for naming conventions) is actinolitic to winchitic at lower temperature, becoming more barroisitic to higher temperature and lower pressure, the actinolite-hornblende solvus closing at around 600 °C. The pseudosection shows two invariant points, with several univariant lines emanating from them. Divariant fields meet along these lines, and they are separated by trivariant fields. Amphibole-bearing assemblages give way to talc-bearing as-

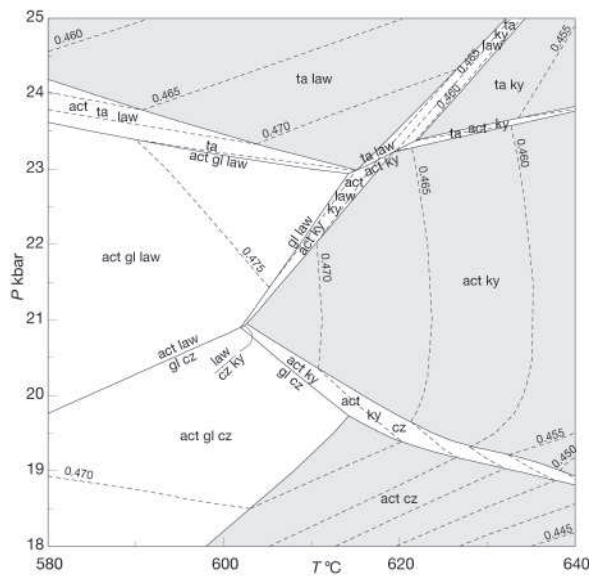


FIGURE 6. A calculated pseudosection for the MORB bulk composition (taken from Sun and McDonough 1989) neglecting Fe_2O_3 and TiO_2 (SiO_2 53.40, Al_2O_3 9.26, CaO 12.43, MgO 12.93, FeO 8.29, Na_2O 2.66). The phases are lawsonite (law), talc (ta), calcic amphibole (act), glaucophane (gl), kyanite (ky), clinozoisite (cz), in addition to garnet, omphacite, quartz, and H_2O . Dashed lines are contours of jadeite mole fraction in pyroxene.

semblages above 23–24 kbar pressure, while lawsonite eclogites occur only in the high-pressure and low-temperature parts of the diagram. Kyanite eclogites occur in the higher temperature parts of the diagram, with either amphibole (lower pressures) or talc (higher pressures). The jadeite content of the pyroxenes is restricted to the range 0.45–0.47 corresponding to ordered $P2/n$ omphacites.

Addition of Fe_2O_3 to Figure 6, as in Figure 7, causes the invariant points to become univariant lines, the univariant lines to become divariant fields and the divariant fields to become trivariant fields. The univariant lines formed from the invariant points in Figure 6 do not appear on Figure 7 because there is an inversion of topology about an invariant point at 22 kbar and 605 °C, where these two univariants intersect. Other univariant lines emanating from this invariant point feature in Figure 7. The divariants that meet along these lines include ones that correspond to univariants in Figure 6, as well as new ones relating to the new topology. The broad features from Figure 6 carry over to Figure 7, with calcic amphiboles stable up to around 22 kbar, giving way to lawsonite-bearing assemblages (at low temperatures) and talc-kyanite-bearing assemblages (at higher temperatures). The combined jadeite + acmite mole fractions of pyroxene show a very slightly larger range (0.44–0.48) than the jadeite contents for the ferric-free system, with the acmite content remaining approximately constant (at X_{acm} around 0.06) over the P - T range of Figure 7.

With changing oxidation state from completely reduced through that corresponding to the analyzed composition to more oxidized states, the divariants involving talc will sweep down

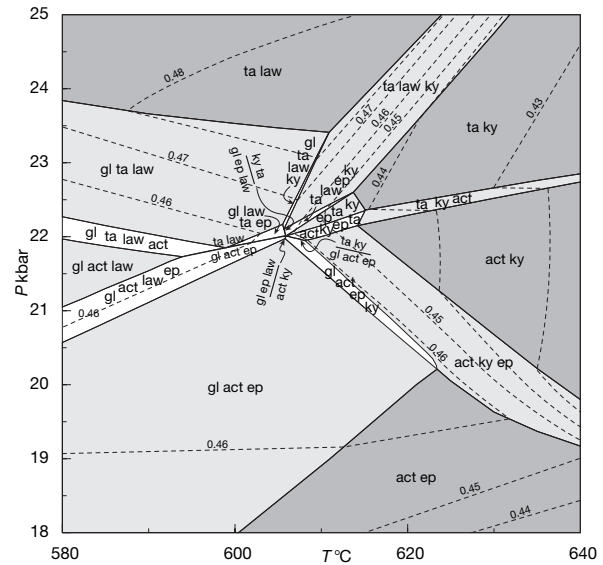


FIGURE 7. A calculated pseudosection for ferric-bearing MORB bulk composition (taken from Sun and McDonough 1989); SiO_2 53.40, Al_2O_3 9.26, CaO 12.43, MgO 12.93, FeO 8.29, Na_2O 2.66, TiO_2 1.07, O 0.50. The phases are lawsonite (law), talc (ta), calcic amphibole (act), glaucophane (gl), kyanite (ky), epidote (ep) in addition to garnet, omphacite, rutile, quartz, and H_2O . Dashed lines are contours of combined jadeite + acmite mole fraction in pyroxene.

pressure, whereas those involving epidote will sweep up pressure. For a series of rocks forming in a particular small P - T range, this means that there is the possibility of a considerable variety of eclogite mineral assemblages being produced with varying oxidation state for the MORB composition. Indeed other small changes of bulk composition, involving say the plagioclase substitution, variation of alumina content or Fe-Mg exchange, will also tend to have a dramatic effect on the mineral assemblages, extending the possible variety to include paragonite-bearing and other assemblages. In the context of mineral assemblages that are dominated by garnet and omphacite (i.e., eclogites), a characteristic feature of “hydrous” eclogites is the considerable variety of combinations of minerals such as lawsonite, glaucophane, actinolite, talc, paragonite, epidote, kyanite, and quartz, and the modeling predicts this variety.

At the conditions of the invariant point in Figure 7, the omphacite has composition $\text{Jd}_{40}\text{Di}_{47}\text{Hed}_{07}\text{Ac}_{06}$, and coexists with glaucophane with $X_{\text{M}_2\text{Fe}^{3+}} = 0.07$, calcic amphibole with $X_{\text{M}_2\text{Fe}^{3+}} = 0.03$ and epidote of composition $\text{Cz}_{89}\text{Ep}_{11}$. Thus the ferric to aluminum ratios of sodic amphiboles and omphacite are similar and higher than calcic amphibole, but all are less ferric than the coexisting epidote, in broad agreement with those seen in natural eclogites. It will be a fruitful future exercise to refine the models for amphibole, omphacite and epidote to match the partitions in more detail.

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APPENDIX

The model is made up of an independent set of end-members, which allows a complete description of the thermodynamic behavior of clinopyroxenes within that compositional space given by the Gibbs free energy

$$G_{\text{cpx}} = \sum_{i=1}^n p_i (G_i^\circ + RT \ln a_i^{\text{ideal}} + RT \ln \gamma_i)$$

in which G_{cpx} is the Gibbs energy of the pyroxene; G_i° is the Gibbs energy of pure end-member i ; a_i^{ideal} is the ideal-mixing activity of i in the pyroxene; γ_i is the activity coefficient of i ; p_i is the proportion of i ; and n is the number of end-members in the independent set.

The activity coefficients are found from the symmetric formalism (macroscopic regular solution) expression:

$$RT \ln \gamma_k = - \sum_i \sum_{j>i} (\delta_i - p_i)(\delta_j - p_j) W_{ij}$$

In the expression above $\delta_i = 1$ if $i = k$ and $\delta_i = 0$ if $i \neq k$, and W_{ij} is the macroscopic interaction energy between end-members i and j . Or alternatively, summing the non-ideal terms

$$\sum_{i=1}^n p_i (RT \ln \gamma_i) = \sum_i \sum_{j>i} p_i p_j W_{ij}$$

The thermodynamic data used for calculations in this paper are based on Holland and Powell (1998) and recent updates, specifically the file tcads55.txt available from the TJBH website (<http://www.esc.cam.ac.uk/astaff/holland/>) or from the RP site (<http://www.earthsci.unimelb.edu.au/tpg/thermocalc/>). Activity-composition models for amphiboles are from Diener et al. (in prep) and are extended from those in Dale et al. (2005) in allowing Fe-Mg ordering. Models for talc and epidote are taken from Holland and Powell (1998). Models for omphacite are described in this paper and are given below for the NCFMAF'S system. THERMOCALC coding for omphacite and amphibole will be available from the web sites above.

The variables to describe the composition and ordering for the end-members jd-di-om-om1-hed-cfm-acm-jac are:

$$f = (X_{\text{Fe}^{3+}}^{\text{M1m}} + X_{\text{Fe}^{3+}}^{\text{M1a}}) / (X_{\text{Fe}^{3+}}^{\text{M1m}} + X_{\text{Fe}^{3+}}^{\text{M1a}} + X_{\text{Al}}^{\text{M1m}} + X_{\text{Al}}^{\text{M1a}})$$

$$x = (X_{\text{Fe}}^{\text{M1m}} + X_{\text{Fe}}^{\text{M1a}}) / (X_{\text{Fe}}^{\text{M1m}} + X_{\text{Fe}}^{\text{M1a}} + X_{\text{Mg}}^{\text{M1m}} + X_{\text{Mg}}^{\text{M1a}})$$

$$j = (X_{\text{Na}}^{\text{M2c}} + X_{\text{Na}}^{\text{M2n}}) / 2$$

$$Q_1 = (X_{\text{Al}}^{\text{M1a}} - X_{\text{Al}}^{\text{M1m}}) / 2$$

$$Q_2 = (X_{\text{Na}}^{\text{M2n}} - X_{\text{Na}}^{\text{M2c}}) / 2$$

$$Q_{\text{af}} = (X_{\text{Fe}^{3+}}^{\text{M1a}} - X_{\text{Fe}^{3+}}^{\text{M1m}}) / 2$$

$$Q_{\text{fm}} = X_{\text{Fe}}^{\text{M1a}} / (X_{\text{Fe}}^{\text{M1a}} + X_{\text{Mg}}^{\text{M1a}}) - x$$

To set the proportion of om1 to zero, we set $Q_1 = Q_2 - Q_{af}$, the site fractions become, in terms of Q ($= Q_2$):

$$x_{Mg}^{M1m} = (1-j+Q)(1-x+Q_{fm}) - 2QQ_{fm}$$

$$x_{Fe}^{M1m} = (1-j+Q)(x-Q_{fm}) + 2QQ_{fm}$$

$$x_{Fe^{3+}}^{M1m} = fj - Q_{af}$$

$$x_{Al}^{M1m} = j(1-f) - Q + Q_{af}$$

$$x_{Mg}^{M1a} = (1-j-Q)(1-x-Q_{fm})$$

$$x_{Fe}^{M1a} = (1-j-Q)(x+Q_{fm})$$

$$x_{Fe^{3+}}^{M1a} = fj + Q_{af}$$

$$x_{Al}^{M1a} = j(1-f) + Q - Q_{af}$$

$$x_{Na}^{M2c} = j - Q$$

$$x_{Ca}^{M2c} = 1 - j + Q$$

$$x_{Na}^{M2n} = j + Q$$

$$x_{Ca}^{M2n} = 1 - j - Q$$

and the proportions of the end-members are

$$p_{jd} = j(1-f) - Q - Q_{af}$$

$$p_{di} = (1-j-Q)(1-x+Q_{fm}) - 2Qx$$

$$p_{hed} = (1-j-Q)(x+Q_{fm})$$

$$p_{om} = 2Q$$

$$p_{cfm} = 2Qx + 2Q_{fm}(j-1+Q)$$

$$p_{acm} = fj - Q_{af}$$

$$p_{jac} = 2Q_{af}$$

The ideal end-member activities are given by:

$$a_{jd} = \left(X_{Al}^{M1m} X_{Al}^{M1a} X_{Na}^{M2c} X_{Na}^{M2n} \right)^{\frac{1}{2}}$$

$$a_{di} = \left(X_{Mg}^{M1m} X_{Mg}^{M1a} X_{Ca}^{M2c} X_{Ca}^{M2n} \right)^{\frac{1}{2}}$$

$$a_{hed} = \left(X_{Fe}^{M1m} X_{Fe}^{M1a} X_{Ca}^{M2c} X_{Ca}^{M2n} \right)^{\frac{1}{2}}$$

$$a_{acm} = \left(X_{Fe^{3+}}^{M1m} X_{Fe^{3+}}^{M1a} X_{Na}^{M2c} X_{Na}^{M2n} \right)^{\frac{1}{2}}$$

$$a_{om} = \left(X_{Mg}^{M1m} X_{Al}^{M1a} X_{Ca}^{M2c} X_{Na}^{M2n} \right)^{\frac{1}{2}}$$

$$a_{cfm} = \left(X_{Fe}^{M1m} X_{Mg}^{M1a} X_{Ca}^{M2c} X_{Ca}^{M2n} \right)^{\frac{1}{2}}$$

$$a_{jac} = \left(X_{Al}^{M1m} X_{Fe^{3+}}^{M1a} X_{Na}^{M2c} X_{Na}^{M2n} \right)^{\frac{1}{2}}$$

The complete set of model interaction energies, excluding all dependent end-members, for the NCFMAF'S system are in Table 3 in text.

The enthalpies for the ordering reactions for each ordered end-member in the complete independent set are:

$$\Delta H_R^{om} = 2H_{om} - H_{jd} - H_{di} = -5.6 \pm 0.4 \text{ kJ}$$

$$\Delta H_R^{cfm} = 2H_{cfm} - H_{di} - H_{hed} = -3.0 \pm 1 \text{ kJ}$$

$$\Delta H_R^{jac} = 2H_{jac} - H_{jd} - H_{acm} = -2.0 \pm 2 \text{ kJ}$$