

# Mineral activity–composition relations and petrological calculations involving cation equipartition in multisite minerals: a logical inconsistency

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**ABSTRACT** Equipartition is an assumption that preserves the same relative fraction of the cations on each site, originally used just to distribute cations such as Fe and Mg over two or more sites during mineral recalculation. This approximation has been used in almost all thermometry and barometry applications in petrology involving pyroxene, amphibole, chlorite and biotite mica. It has also become the default approach used in deriving activity–composition relations in multisite minerals where details of element partitioning among the sites is unknown and therefore assumed to be random. It is shown that, where a third element, such as Al, resides on just one of the sites, equipartition introduces a serious logical and numerical inconsistency between the enthalpy and entropy of mixing. In particular, application of equipartition is demonstrated to be equivalent to treating the solution as one in which all cations reside on one type of site. For example, in the case of aluminous orthopyroxene the equipartition assumption implies that Fe, Mg and Al are distributed across two identical sites, and that end-members such as Mg-tschermak's pyroxene have enthalpies characterized by a totally disordered distribution of Mg and Al over the M2 and M1 sites. Clearly this is unsupportable, and solid solutions should be treated with appropriate thermodynamics for order–disorder. For phases where element partitioning data are unavailable, we offer a simple alternative strategy, using the ordering of Fe and Mg on M1 and M2 sites in biotite as an example.

**Key words:** activity, biotite, equipartition, pyroxene, site-distribution, thermodynamic.

## INTRODUCTION: EQUIPARTITION IN ACTIVITY–COMPOSITION MODELS

Thermodynamics of mixing in ferromagnesian silicates have provided invaluable tools for determining the conditions of formation of rocks in the Earth's crust and upper mantle (Wood & Banno, 1973; Ferry & Spear, 1978; Newton & Haselton, 1981; Powell, 1985a,b; Powell & Holland, 1988; Essene, 1989). A key assumption in many instances has been the use of ideal mixing of cations on crystal sites, and the approach has been remarkably successful in deriving reasonably reliable temperatures and pressures for metamorphic rocks. However recent advances in experimental and theoretical mineralogy have shown that even cations with similar size and identical charge, such as Fe and Mg, mix with appreciable non-ideality on sites. In addition, experimental studies on Fe–Mg orthopyroxene have shown that Fe partitions with a preference for the larger M2 site whereas Mg is concentrated into the smaller M1 site (Saxena & Ghose, 1971; Besançon, 1981; Grammenopoulou, 1981 (in Anovitz *et al.*, 1988); Anovitz *et al.*, 1988; Molin *et al.*, 1991; Skogby, 1992; Yang & Ghose, 1994; Stimpfl *et al.*, 1999).

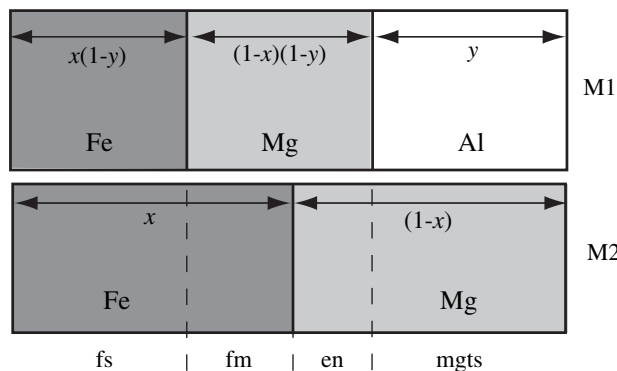
There exist no data on intracrystalline partitioning for the many minerals of interest to petrologists who wish to use thermodynamic datasets to calculate temperatures and pressures for natural rocks or to construct phase diagrams to interpret the textures seen in them. In such cases, the assumption usually made is that Fe and Mg partition equally among the sites available, even though non-ideality is known to be quite significant in the mixing of other cations within the same sites – for example, Ca–Mg–Fe mixing on the M1 and M2 sites in clino- and orthopyroxene. This assumption (equipartition) becomes explicit in the datafile coding for software like THERMOCALC, although users may well be unaware of it. It is the default option in almost all thermodynamic calculations in petrology, particularly in thermobarometry involving pyroxene, amphibole, mica and chlorite. Some familiar examples in which intracrystalline Fe–Mg site distributions are not accounted for are: orthopyroxene, in garnet–orthopyroxene and orthopyroxene–spinel thermometry and barometry (e.g. Droop & Bucher-Nurminen, 1984; Harley, 1984; Perkins & Chipera, 1985; Lee & Ganguly, 1988; Carswell & Harley, 1990; Berman & Aranovich, 1996; Aranovich & Berman, 1997;

Liermann & Ganguly, 2003; Pattison *et al.*, 2003; Dasgupta *et al.*, 2004); clinopyroxene, in garnet–clinopyroxene and clinopyroxene–orthopyroxene thermometry (e.g. Wood & Banno, 1973; Ellis & Green, 1979; Powell, 1985a; Brey *et al.*, 1986; Fonarev *et al.*, 1991; Berman *et al.*, 1995; Ravna, 2000); amphibole, coexisting with garnet in thermometry and barometry (e.g. Graham & Powell, 1984; Kohn & Spear, 1989, 1990; Holland & Blundy, 1994; Dale *et al.*, 2000); biotite, in garnet–biotite thermometry and barometry (e.g. Ferry & Spear, 1978; Ganguly & Saxena, 1984; Kleemann & Reinhardt, 1994; Gessmann *et al.*, 1997; Holdaway, 2000); chlorite, in various metamorphic reactions (e.g. Dickenson & Hewitt, 1986; Holland *et al.*, 1998; Vidal *et al.*, 2001, 2005); also combinations of phases in many petrological publications which have used the software THERMOCALC (Powell & Holland, 1988) or PERPLEX (Connolly, 1990) together with the thermodynamic dataset of Holland & Powell (1998) or Berman (1988).

In minerals where there is no information available on partitioning of elements, say Mg and Fe, between different sites, the traditional mineral thermobarometric approach has been to allocate cations in proportion to that of the bulk mineral. Allocation of Fe and Mg between M1 and M2 sites of such a two-site mineral would usually be calculated (e.g. Powell, 1978) from

$$\left(\frac{\text{Fe}}{\text{Fe} + \text{Mg}}\right)_{\text{M1}} = \left(\frac{\text{Fe}}{\text{Fe} + \text{Mg}}\right)_{\text{M2}} = \left(\frac{\text{Fe}}{\text{Fe} + \text{Mg}}\right)_{\text{phase}} \equiv x.$$

This method of allocating cations to sites is illustrated in Fig. 1 which shows a two-site mineral in which Al resides solely on M1 (Molin, 1989) and Fe and Mg are assumed to be equipartitioned across the two sites. In this description of the mineral there are just two macroscopic composition parameters



**Fig. 1.** Site box diagram for orthopyroxene (and other Fe–Mg–Al minerals with two sites, in which Al occupies only the M1 site), showing equipartition of Fe and Mg ( $x = \text{Fe}/(\text{Fe} + \text{Mg}) = 0.5$ ) across the sites. Implicit proportions of end-members are shown, in which an ordered FeMg end-member is apparent. End-members are: en = Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, fs = Fe<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, fm = FeMgSi<sub>2</sub>O<sub>6</sub>, mgts = MgAlSiAlO<sub>6</sub> and fm = FeMgSi<sub>2</sub>O<sub>6</sub>.

$$y = x_{\text{Al}}^{\text{M1}} \quad \text{and} \quad x = \frac{\text{Fe}}{\text{Fe} + \text{Mg}}.$$

Site box diagrams, such as Fig. 1, are useful for displaying site distributions of cations on the two sites, and in these diagrams the proportions of the various end-members may be read off visually by lining up the two site boxes one above the other. In what follows, the mineral orthopyroxene will be used as an example of a typical two-site phase. The proportion of an end-member such as Mg-Tschermaks pyroxene (mgts, Mg<sub>M2</sub>Al<sub>M1</sub>) is given by the overlap of Mg in box M2 and Al in box M1 ( $p_{\text{mgts}} = y$ ). The site fractions, using the equipartition assumption, are

$$\begin{aligned} x_{\text{AlM1}} &= y \\ x_{\text{FeM1}} &= x(1-y) \\ x_{\text{MgM1}} &= (1-x)(1-y) \\ x_{\text{FeM2}} &= x \\ x_{\text{MgM2}} &= 1-x \end{aligned}$$

The thermodynamics of a mineral such as orthopyroxene, illustrated in Fig. 1, are usually expressed by describing the activities of the end-members as the sum of an ideal entropic component and a separate non-ideal enthalpic component. The entropic component yields ideal activities for an end-member such as mgts:

$$RT \ln a_{\text{mgts}}^{\text{ideal}} = RT \ln x_{\text{Mg}}^{\text{M2}} x_{\text{Al}}^{\text{M1}}$$

For the purposes of this paper, we follow Wood & Banno (1973) in ignoring the tetrahedral site terms in orthopyroxene. The non-ideal enthalpic part is added on, using a model such as the symmetric formalism (Powell & Holland, 1993), as

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

in which  $p_i$  is the proportion of end-member  $i$  in phase  $k$ ,  $p_i^\circ$  is the proportion  $p_i$  of end-member  $i$  in pure  $k$ , and  $W_{ij}$  is a symmetrical macroscopic interaction parameter for the  $ij$  binary. The summations are over an independent set of end-members chosen to represent the composition of the phase. This set can be observed via a site box diagram, being sufficient to represent the site distributions. The activity of mgts is then expressed as the sum of the ideal and non-ideal components,

$$\begin{aligned} RT \ln a_{\text{mgts}} &= RT \ln a_{\text{mgts}}^{\text{ideal}} + RT \ln \gamma_{\text{mgts}} \\ &= (1 - p_{\text{mgts}}) p_{\text{en}} W_{\text{mgts en}} \\ &\quad + (1 - p_{\text{mgts}}) p_{\text{fs}} W_{\text{mgts fs}} - p_{\text{fs}} p_{\text{en}} W_{\text{fs en}} \end{aligned}$$

The proportions of the end-members needed for writing the macroscopic activity coefficients above can be found by solving the set of three mass balance equations relating old components (Al, Fe, Mg) to new components (mgts, fs, en):

$$\begin{array}{l}
 \text{Al} \\
 \text{Fe} \\
 \text{Mg}
 \end{array}
 \begin{pmatrix}
 \text{mgts} & \text{fs} & \text{en} \\
 1 & 0 & 0 \\
 0 & 2 & 0 \\
 1 & 0 & 2
 \end{pmatrix}
 \cdot
 \begin{pmatrix}
 p_{\text{mgts}} \\
 p_{\text{fs}} \\
 p_{\text{en}}
 \end{pmatrix}
 =
 \begin{pmatrix}
 y \\
 x + x(1 - y) \\
 (1 - x) + (1 - x)(1 - y)
 \end{pmatrix}
 \quad (1)$$

in which the three rows on the left hand side are the compositions of the end-members and the three rows on the right hand side are the total amounts of octahedral Al, Fe and Mg given by the site fraction expressions. The solution of these equations yields

$$\begin{aligned}
 p_{\text{mgts}} &= y \\
 p_{\text{fs}} &= \frac{x}{2}(2 - y) \\
 p_{\text{en}} &= 1 - y - \frac{x}{2}(2 - y)
 \end{aligned}$$

The equipartition assumptions described above form the basis of almost all applications of orthopyroxene thermometry and barometry in aluminous systems. The advantages of assuming equipartition appear to be that (a) it keeps the algebra very simple, (b) it requires no additional ordered end-members, and hence additional non-ideal interaction energy terms and (c) it needs no solution of a nonlinear equation to determine the equilibrium site distribution at every temperature. Unsurprisingly this has been a popular way to proceed. In the example used above, the equipartition assumption needs only three end-members and three non-ideal interaction energies, whereas a full ordering model would require four end-members and six non-ideal interaction energies, and determining these extra energy quantities can be a non-trivial task. However, as the reader may have noticed, there is a serious problem with the equipartition assumption because the proportions, as written out above, do not agree with the site box diagram (Fig. 1). The main purpose of this paper is to examine the basis for this inconsistency and its implications for petrological calculations.

### THERMODYNAMIC INCONSISTENCIES IN THE EQUIPARTITION ASSUMPTION

The first and most obvious inconsistency can be seen in Fig. 1 where the box diagram shows that there is a significant proportion of an additional ordered fm end-member [from the diagram  $p_{\text{fm}} = x - x(1 - y) = xy$ ]. But, under equipartition, the end-member fm is not even considered, its amount being implicitly hidden in the incorrect proportions of the other end-members. Doing this appears benign until the energetic consequences are considered, and we will show that it also introduces bias in the calculation of pressures and

temperatures of rocks and in the location of features on phase diagrams. Avoiding the end-member mgts might seem desirable, and several studies (e.g. Lee & Ganguly, 1988; Aranovich & Berman, 1997) have used a simple ternary mixing model composed of enstatite (MgMg), ferrosilite (FeFe) and orthocorundum (AlAl) end-members, yet this also assumes complete Al-Mg-Fe distribution across both sites. Although it has the benefit of being self-consistent (the entropy of mixing also assumes the same random distribution), it is a model which suffers the same equipartition assumption drawbacks. Because this model involves a disordered state with a large entropy of mixing, it also requires a large compensating enthalpy of mixing too.

The thermodynamics of order-disorder in a two-site phase will now be briefly reviewed to make comparisons with, and highlight the problems of, the equipartition model. We will continue to use orthopyroxene as the example for discussion because it is a simple two-site phase for which Fe-Mg partitioning is well known from experimental studies, and whose thermodynamics have been much discussed already (e.g. Sack, 1980; Chatillon-Colinet *et al.*, 1983; Carpenter & Salje, 1994; Kroll *et al.*, 1994; Sack & Ghiorso, 1994; Stimpfl *et al.*, 1999, and the approach to be used here has been summarized in Holland & Powell, 1996a,b).

Considering aluminous orthopyroxene, in which Al is assumed to reside solely on the M1 site (Molin, 1989), the complete set of end-members are en ( $\text{Mg}_2\text{Si}_2\text{O}_6$ ), fs ( $\text{Fe}_2\text{Si}_2\text{O}_6$ ), fm ( $\text{FeMgSi}_2\text{O}_6$ ), mgts ( $\text{MgAlSiAlO}_6$ ) and fets ( $\text{FeAlSiAlO}_6$ ) with site distributions as in Table 1 (ignoring tetrahedral site mixing for simplicity).

Only four end-members are required to make up an independent set, and, if the thermodynamics are formulated correctly, the choice is immaterial. Here we use the set en-fs-fm-mgts. The site fractions, in terms of

$$x = \left( \frac{\text{Fe}}{\text{Fe} + \text{Mg}} \right)_{\text{opx}}, \quad y = x_{\text{Al}}^{\text{M1}}$$

and the order parameter,  $Q = 2(x_{\text{Fe}}^{\text{M2}} - x)$ , are:

$$\begin{aligned}
 x_{\text{AlM1}} &= y \\
 x_{\text{FeM1}} &= x(1 - y) - \frac{1}{2}Q \\
 x_{\text{MgM1}} &= (1 - x)(1 - y) + \frac{1}{2}Q \\
 x_{\text{FeM2}} &= x + \frac{1}{2}Q \\
 x_{\text{MgM2}} &= 1 - x - \frac{1}{2}Q
 \end{aligned}$$

**Table 1.** End-members and site distribution in aluminous opx

	M2	M1
en	Mg	Mg
fs	Fe	Fe
fm	Fe	Mg
mgts	Mg	Al
fets	Fe	Al

and the proportions of the end-members in the independent set are

$$\begin{aligned} p_{\text{mgts}} &= y \\ p_{\text{en}} &= 1 - x - y - \frac{1}{2}Q \\ p_{\text{fs}} &= x(1 - y) - \frac{1}{2}Q \\ p_{\text{fm}} &= xy + Q \end{aligned} \quad (2)$$

The usual practice in applying equipartition is seen to be equivalent to setting  $Q$  to zero in the site fraction expressions above. This deals effectively with the entropic part of the mixing, as can be seen by comparing the site fractions above with those for equipartition. However, setting  $Q$  to zero in the end-member proportions above does not zero the *proportion* of the ordered end-member fm, but sets  $p_{\text{fm}} = xy$ . Thus the system is not reduced in dimension by setting  $Q$  to zero. The order parameter under the equipartition approach is implicitly given by the composition of the pyroxene,  $Q = -xy$ , which is physically unreasonable, as well as giving strange site fractions on substitution in the above equations. Setting  $Q$  to different things for the entropic and enthalpic parts is inconsistent thermodynamically and is unsupportable. In the next sections, the harmful thermodynamic consequences of equipartition on the energetics of solid solutions are considered.

### Consequences of equipartition on energetics

Because the whole Gibbs energy surface of the phase is expressed in terms of mixing of the end-members in the independent set, the Gibbs energy of other pure end-members (in this case, specifically, fets), are completely specified. Some of the energetic consequences of equipartition are only apparent when the thermodynamic properties of the fets end-member are derived, using the energetic relationships in an independent set. For the full order–disorder model the equivalences (Powell & Holland, 1999) are

$$\begin{aligned} W_{\text{en fets}}^{\text{od}} &= 2W_{\text{en fm}} + 2W_{\text{en mgts}} - W_{\text{fm mgts}} \\ W_{\text{fm fets}}^{\text{od}} &= W_{\text{en mgts}} \\ W_{\text{fs fets}}^{\text{od}} &= W_{\text{en fm}} - W_{\text{en fs}} + W_{\text{en mgts}} - W_{\text{fm mgts}} \\ &\quad + W_{\text{fs fm}} + W_{\text{fs mgts}} \\ W_{\text{mgts fets}}^{\text{od}} &= W_{\text{en fm}} \\ G_{\text{fets}}^{\text{od}} &= -G_{\text{en}} + G_{\text{fm}} + G_{\text{mgts}} - W_{\text{en fm}} - W_{\text{en mgts}} \\ &\quad + W_{\text{fm mgts}} \end{aligned}$$

The first four lines above give the relationships among the interaction energies between the fifth end-member fets and the four chosen independent end-members, and the last line gives the Gibbs energy of the fets end-member.

The ordering reaction in the Al-free pyroxene,  $\text{en} + \text{fs} = 2\text{fm}$ , is characterized by an enthalpy change  $\Delta H_{\text{R}}$ , which on rearrangement gives

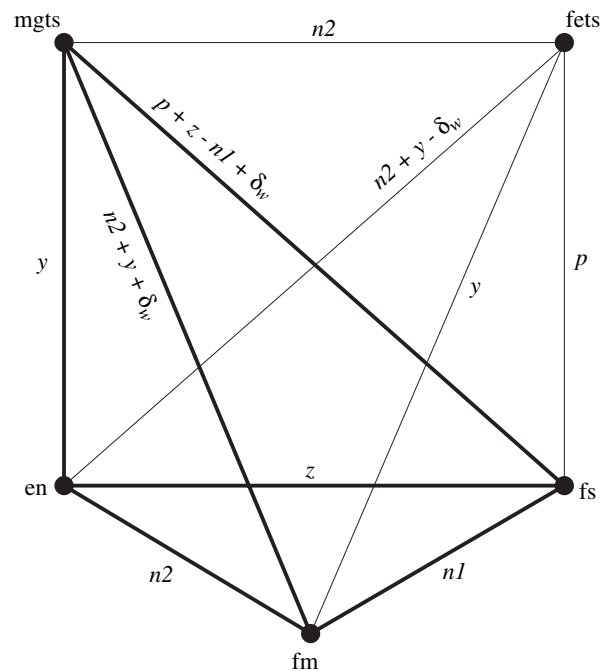
$$G_{\text{fm}} = \frac{1}{2}G_{\text{en}} + \frac{1}{2}G_{\text{fs}} + \frac{1}{2}\Delta H_{\text{R}}$$

Combining this with the relation for the Gibbs energy of the fets end-member above gives

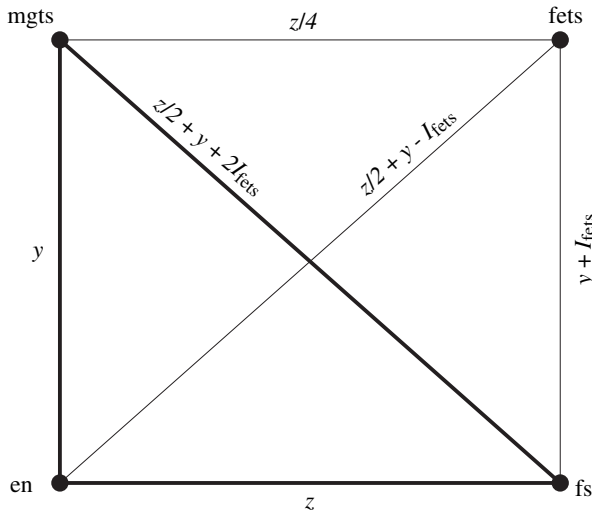
$$G_{\text{fets}}^{\text{od}} = G_{\text{mgts}} - \frac{1}{2}G_{\text{en}} + \frac{1}{2}G_{\text{fs}} + \frac{1}{2}\Delta H_{\text{R}} + \delta_{\text{w}}$$

where  $\delta_{\text{w}} = -W_{\text{en fm}} - W_{\text{en mgts}} + W_{\text{fm mgts}}$ . This means that the enthalpy of the fets end-member depends on the magnitude of both the ordering enthalpy  $\Delta H_{\text{R}}$  and the interaction energies  $\delta_{\text{w}}$  associated with ordering in Fe–Mg pyroxene. These energies, which are quite large, are not taken into consideration under equipartition, and lead to incorrect properties of the fets end-member. The sum  $I_{\text{fets}} = (1/2)\Delta H_{\text{R}} + \delta_{\text{w}}$  is the additional energy of fets relative to the linear combination of the end-members mgts, en and fs. Using the values taken from Holland & Powell (1996b) gives an increment to the fets end-member of  $I_{\text{fets}} = -10.25 \text{ kJ mol}^{-1}$  ( $\Delta H_{\text{R}} = -13.9$  and  $\delta_{\text{w}} = -3.3$ ). These energy relationships are summarized in the interaction energy diagram for the order–disorder model in Fig. 2.  $I_{\text{fets}}$ , dominated by the large ordering energy contribution  $\Delta H_{\text{R}}$ , is quite capable of perturbing the calculated phase relations involving the fets end-member, as shown later in Fig. 4.

In contrast to these results, the comparable set of relations, derived under *equipartition*, gives the equivalences involving fets as



**Fig. 2.** Interaction energy diagram for the full order–disorder model, showing interrelationships. For the model used here, from Holland & Powell (1996b), the values for the  $W$ 's are:  $n1 = n2 = 4.5$ ,  $y = p = 0$ ,  $z = 6.8$ ,  $\Delta H_{\text{R}} = -13.9$ ,  $\delta_{\text{w}} = -3.3 \text{ kJ mol}^{-1}$ . Bold lines connect the end-members in the chosen independent set.



**Fig. 3.** Interaction energy diagram for the equipartition model, showing interrelationships. In relation to the terms in the full order-disorder model (Fig. 2)  $z = n_1 + n_2$  and  $\delta_w = 0$ , and with no ordering,  $\Delta H_R = 0$ . Bold lines connect the end-members in the independent set used.

$$W_{\text{en fets}}^{\text{equi}} = \frac{3}{4}W_{\text{en fs}} + \frac{3}{2}W_{\text{en mgts}} - \frac{1}{2}W_{\text{fs mgts}}$$

$$W_{\text{fs fets}}^{\text{equi}} = -\frac{1}{4}W_{\text{en fs}} + \frac{1}{2}W_{\text{en mgts}} + \frac{1}{2}W_{\text{fs mgts}}$$

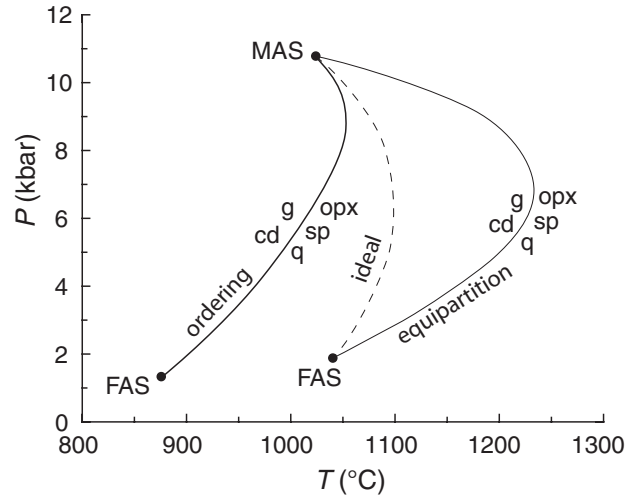
$$W_{\text{mgts fets}}^{\text{equi}} = \frac{1}{4}W_{\text{en fs}}$$

$$G_{\text{fets}}^{\text{equi}} = -\frac{1}{2}G_{\text{en}} + \frac{1}{2}G_{\text{fs}} + G_{\text{mgts}} - \frac{1}{4}W_{\text{en fs}} - \frac{1}{2}W_{\text{en mgts}} + \frac{1}{2}W_{\text{fs mgts}}$$

These relationships are depicted in the interaction energy diagram for equipartition (Fig. 3). The third expression  $W_{\text{mgts fets}}^{\text{equi}} = (1/4)W_{\text{en fs}}$  above, in particular, is a counter-intuitive and thermodynamically illogical result: the mgts-fets solution involves only half the number of Fe-Mg substitutions as the en-fs solution, and we should therefore expect  $W_{\text{mgts fets}}$  to be  $(1/2)W_{\text{en fs}}$  to reflect this. The intuitive, and correct, result is given by the expression for  $W_{\text{mgts fets}}^{\text{od}}$  earlier. Further, if strain energies can be ignored, the macroscopic interaction energies can be compared with the sum of their microscopic terms (e.g. Powell & Holland, 1993), as follows

$$W_{\text{mgts fets}}^{\text{equi}} = \frac{1}{4}W_{\text{en fs}} = \frac{1}{4}(W_{\text{MgFe}}^{\text{M1}} + W_{\text{MgFe}}^{\text{M2}} + W_{\text{MgFe}}^{\text{M1M2}})$$

There is a disquieting thing about this:  $W_{\text{mgts fets}}$  involves M1 site Fe-Mg contributions on a join (mgts-fets) in which mixing is supposed to occur only on M2 (M1 is solely occupied by Al in this binary). This flags that Al is not being considered to be just on M1; in fact equipartition implies that Al is distributed *equally* between M1 and M2: equipartition of Fe and Mg is thus forcing Al to equipartition as well. This can be approached in several ways. The first is that the derivation of proportions in Eq. (1) does not preclude the logic applying to a disordered Mg-Tschermak's



**Fig. 4.** *PT* projection in FMAS of the reaction  $g + cd = \text{opx} + \text{sp} + q$ , with the abbreviations,  $g$  = garnet,  $cd$  = cordierite,  $\text{opx}$  = orthopyroxene,  $\text{sp}$  = spinel and  $q$  = quartz. Use of equipartition displaces the curve progressively to higher temperature as the minerals become more Fe-rich. The calculated position of the FAS invariant point is shifted to higher  $T$  because the free energy of the fets end-member is different in the equipartition case.

pyroxene (dts), with Al equally distributed between the M1 and M2 sites. This is because in Eq. (1), the macroscopic composition of the end-member is used, and mgts and dts have the same macroscopic composition. The second is to see that self-evidently a box diagram drawn involving dts, and not mgts, has no fm end-member under the equipartition assumption. The third is to treat the distribution of Al between M1 and M2 as itself an order-disorder problem. In full order-disorder form, with  $Q_a = x_{\text{Al,M1}} - x_{\text{Al,M2}}$  and  $Q = 2(x_{\text{Fe,M2}} / (x_{\text{Mg,M2}} + x_{\text{Fe,M2}}) - x)$ , the proportions are:

$$\begin{aligned} p_{\text{en}} &= 1 - x - y - \frac{Q}{2} + \frac{1}{4}(Q + 2x)(y - Q_a) \\ p_{\text{fs}} &= x(1 - y) - \frac{Q}{2} + \frac{1}{4}(Q + 2x)(y - Q_a) \\ p_{\text{fm}} &= xy + Q - \frac{1}{2}(Q + 2x)(y - Q_a) \\ p_{\text{mgts}} &= Q_a \\ p_{\text{dts}} &= y - Q_a \end{aligned} \quad (3)$$

Setting  $Q_a = y$  puts all Al on M1, giving identical proportions to Eq. (2), as required:

$$\begin{aligned} p_{\text{mgts}} &= y \\ p_{\text{en}} &= 1 - x - y - \frac{1}{2}Q \\ p_{\text{fs}} &= x(1 - y) - \frac{1}{2}Q \\ p_{\text{fm}} &= xy + Q \\ p_{\text{mgts}} &= y \\ p_{\text{dts}} &= 0 \end{aligned}$$

Now, setting  $Q = 0$  and  $Q_a = 0$  in Eq. (3) assuming equipartition of Fe, Mg and Al, gives for the proportions:

$$\begin{aligned}
 p_{\text{en}} &= 1 - y - x \left(1 - \frac{y}{2}\right) \\
 p_{\text{fs}} &= x \left(1 - \frac{y}{2}\right) \\
 p_{\text{fm}} &= 0 \\
 p_{\text{mgts}} &= 0 \\
 p_{\text{dts}} &= y
 \end{aligned}$$

and these are the same as given by solving Eq. (1), demonstrating that equipartition of Fe and Mg does indeed distribute all three cations equally across the two sites.

The gross logical inconsistency embodied in equipartition is that Al is known to reside on just the M1 site (and this is used in formulating the entropy of mixing), but equipartition forces the enthalpy of mixing to involve Al to be equally distributed between the two sites. Thus, the enthalpy discrepancy between fets in the full order–disorder and the equipartition situations is because the former case involves the ordered end-member  $\text{Fe}_{\text{M2}}\text{Al}_{\text{M1}}\text{AlSiO}_6$ , whereas in the latter, it is the disordered  $(\text{Fe}_{1/2}\text{Al}_{1/2})_{\text{M2}}(\text{Fe}_{1/2}\text{Al}_{1/2})_{\text{M1}}\text{AlSiO}_6$  end-member.

Additionally, as can be seen from Fig. 3 the equipartition equivalences impose very restrictive (and incorrect) constraints on the energetics: first, as already noted above, that  $W_{\text{mgts fets}} = (1/4)W_{\text{en fs}}$ , second that  $W_{\text{fs fets}} = W_{\text{en mgts}} + I_{\text{fets}}$  and third that  $W_{\text{fs mgts}} = (1/2)W_{\text{en fs}} + W_{\text{en mgts}} + 2I_{\text{fets}}$ . With  $I_{\text{fets}}$  being potentially a large negative number, this may force unreasonable negative values for  $W_{\text{fs fets}}$  and particularly  $W_{\text{fs mgts}}$ .

## DISCUSSION

Whereas in the Al-free orthopyroxene it is possible to mimic the energetics of ordering by taking a fictive small value for  $W_{\text{en fs}}$ , this is effectively impossible for Al-bearing orthopyroxene, or indeed any phase in which other elements only reside on some of the sites on which Fe and Mg mix. This is because it is not only the activity–composition relationships that need to be approximated but also the properties of dependent end-members, for example fets in opx.

The practical implications are very clearly shown in Fig. 4, which illustrates the seriousness of the problem, and which shows the effect of using equipartition of Fe and Mg on the M2 and M1 sites in orthopyroxene on a calculated phase diagram. The figure shows the FMAS univariant reaction, garnet + cordierite = orthopyroxene + spinel + quartz, in a *PT* projection. The curve calculated with the full order–disorder orthopyroxene model (the reference curve: Holland & Powell, 1996b; Powell & Holland, 1999) extends from a MAS invariant point at 10.8 kbar and 1023 °C down to the corresponding FAS invariant point at 1.3 kbar and 875 °C. The thermodynamic parameters used for this full model are  $W_{\text{en fs}} = 6.8 \text{ kJ mol}^{-1}$ ,  $W_{\text{en mgts}} =$

$0 \text{ kJ mol}^{-1}$ ,  $W_{\text{en fm}} = 4.5 \text{ kJ mol}^{-1}$ ,  $W_{\text{fs fm}} = 4.5 \text{ kJ mol}^{-1}$ ,  $W_{\text{fm mgts}} = -1.0 \text{ kJ mol}^{-1}$ ,  $W_{\text{fs mgts}} = 1.2 \text{ kJ mol}^{-1}$ , and  $I_{\text{fm}} = -6.95 \text{ kJ mol}^{-1}$ , where  $I_{\text{fm}}$  is the enthalpy increment to the fm end-member relative to  $(\text{en} + \text{fs})/2$ . Also shown are ideal and non-ideal equipartition versions of the calculation which start at the MAS invariant point but begin to deviate strongly as more Fe is put into the system and end up at a calculated FAS invariant point that differs from the reference calculation by over 150 °C.

The mislocation of the FAS invariant point is because the fets end-member in the full order–disorder model has Al only on M1, whereas in the equipartition model fets has Al distributed across both sites, leading to a different model enthalpy. The equipartitioning curve was calculated using a simple ternary mixture of en + mgts + fs with  $W_{\text{en fs}} = 6.8 \text{ kJ mol}^{-1}$ ,  $W_{\text{en mgts}} = 0 \text{ kJ mol}^{-1}$  and  $W_{\text{fs mgts}} = 3.4 \text{ kJ mol}^{-1}$ . An ideal mixing model, shown in Fig. 1, involving the three end-members en + mgts + fs also behaves in the same inconsistent way because the implied fets end-member in the ideal mixing case (still) involves Al distributed across both M1 and M2 sites. A range of curves, between the ideal curve and the equipartition curve shown, could be calculated by reducing the magnitudes of the interaction energies. However, to make an equipartition model approximate the full order–disorder curve would require unrealistically large negative values for some energy terms ( $W_{\text{fs fets}}$  and  $W_{\text{fs mgts}}$ ) to compensate for the missing ordered end-member. This illustrates nicely the fact that the thermodynamic model must be chosen to reflect the energetics of mixing in the structure as known from crystallographic studies – in this case it is known that Al does not reside on M2. If experiments were available on this reaction and a mixing model derived from it by regression using an equipartition model, the energy quantities derived would be seriously in error.

Although the consequences of equipartition lead to severe problems with the thermodynamics of the complete phase, particularly in the energies of dependent end-members, the equipartition assumption does not affect the way that most thermobarometers are used in petrology. This is because the equations use only the activities of one or two end-members, and do not represent the whole thermodynamics of a particular phase. However, any mixing energies ( $W_{ij}$  parameters) produced in calibrating a thermobarometer are only fitting parameters, and will usually be erroneous, for example, not being comparable with calorimetrically determined values.

### Application example: biotite

Having discussed why equipartition fails as an expedient method in dealing with solid solutions of Fe–Mg minerals in which the amount of intracrystalline partitioning is not known, we suggest a method of proceeding which preserves thermodynamic consistency

while minimizing the number of unknowns that need to be determined. Application of an order–disorder model to other minerals is straightforward once the crystal chemistry of the desired mineral is known. In general where non-equivalent sites occur in minerals, Fe will tend to partition into the larger and/or more distorted octahedral site (e.g. Ghose, 1982). Some common silicates are characterized by Fe–Mg mixing on only one type of site and so are capable of description by simple ideal or non-ideal mixing (e.g. regular solution). Among these are chloritoid, carpholite, phengite, cordierite (in which the two sites are symmetry-related and equivalent). Olivine behaves like these because M1 and M2 are very similar in size and shape, and experimental studies show almost no site partitioning (Redfern *et al.*, 2000). Others, like talc, chlorite, amphibole, pyroxene and biotite will require models which do not use equipartition.

Biotite micas will be considered next as an example of how a self-consistent thermodynamic model may be built and calibrated. The crystal chemistry of biotite has been investigated and reviewed recently by Brigatti *et al.* (2000), who showed that this mineral is characterized by three octahedral sites, two regular M2 octahedra and one slightly distorted M1 octahedron. They also showed that Al resides on the M2 sites and that these M2 sites become progressively smaller with increasing Al content of biotite, and that this causes the M1 site to become more distorted and slightly enlarged. As a result, Fe<sup>2+</sup> increasingly prefers the distorted M1 site as Al content rises. This preference is small however, and others (e.g. Takeda & Ross, 1975) found that Mg prefers the M2 sites in different biotite samples. In the thermodynamic model which follows, we show that Fe is predicted to prefer M2 at low Al contents (as in the phlogopite–annite solution series) but changes to prefer M1 in more aluminous biotite. A further complicating factor is Al–Mg ordering on the octahedral sites in biotite. Although X-ray studies show little evidence for Al preferring a single site, the scattering factors for Mg and Al are similar making such ordering difficult to detect. However, Al is known to order strongly onto the M1 site in pyroxene, onto the small M2 site in glaucophane, and onto its own M2a site in omphacite, all as a result of strong Al–Mg ordering. Al also prefers to surround itself with six Mg cations in the analogous trioctahedral sheets of chlorite (Welch *et al.*, 1995). For phlogopite, Circone & Navrotsky (1992) confirmed from IR and Raman spectroscopy that all Al resides on a single M2 site. Thus a fully comprehensive model for biotite probably should allow Al to order onto one of the two M2 sites, splitting the octahedra into M1, M2 and M3 sites, one of which prefers Fe and one preferring Al. However, because Fe–Mg biotite is close to ideal (Wones, 1972; Schullien, 1975), and the details of site distribution are as yet incompletely known, such a complex model is

**Table 2.** End-members and site distribution in biotites

	M12	M3	T1
phl	Mg <sub>2</sub>	Mg	Al Si
ann	Fe <sub>2</sub>	Fe	Al Si
obi	Mg <sub>2</sub>	Fe	Al Si
east	Mg <sub>2</sub>	Al	Al <sub>2</sub>

probably unwarranted, and we shall assume that there are just two types of site in biotite, one M3 site on which Al resides, and two M12 sites, with Fe and Mg partitioned between M3 and M12. In the system K<sub>2</sub>O–FeO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O, an obvious choice of independent end-members involves phlogopite (phl; KMg<sub>3</sub>[AlSi<sub>3</sub>]O<sub>10</sub>(OH)<sub>2</sub>), annite (ann; KFe<sub>3</sub>[AlSi<sub>3</sub>]O<sub>10</sub>(OH)<sub>2</sub>), eastonite (east; KAlMg<sub>2</sub>[Al<sub>2</sub>Si<sub>2</sub>]O<sub>10</sub>(OH)<sub>2</sub>) and ordered biotite (obi; KFeMg<sub>2</sub>[AlSi<sub>3</sub>]O<sub>10</sub>(OH)<sub>2</sub>) as in Table 2. We also assume (following Holland & Powell, 1998) that Al and Si mix on only two of the four tetrahedral sites, which are labelled here as T1.

The thermodynamics are modelled in two stages. First the simpler phlogopite–annite mica is considered, in which complications of octahedral Al are absent, before extending the model to aluminous biotite. For phl–ann micas, involving the hypothetical obi end-member, the site fractions and end-member proportions become, following equations 1 and 2 of Holland & Powell (1996b)

$$\begin{aligned}x_{\text{Fe}}^{\text{M3}} &= x + \frac{2}{3}Q = 1 - p_{\text{phl}} \\x_{\text{Mg}}^{\text{M3}} &= 1 - x - \frac{2}{3}Q = p_{\text{phl}} \\x_{\text{Fe}}^{\text{M12}} &= x - \frac{1}{3}Q = p_{\text{ann}} \\x_{\text{Mg}}^{\text{M12}} &= 1 - x + \frac{1}{3}Q = 1 - p_{\text{ann}}\end{aligned}$$

where  $x$  is the bulk composition Fe/(Fe + Mg) in biotite, and the order parameter  $Q = x_{\text{Fe}}^{\text{M3}} - x_{\text{Fe}}^{\text{M12}}$ .

The ideal mixing on sites activities are given by

$$\begin{aligned}a_{\text{phl}}^{\text{ideal}} &= \left(x_{\text{Mg}}^{\text{M12}}\right)^2 \left(x_{\text{Mg}}^{\text{M3}}\right) \\a_{\text{ann}}^{\text{ideal}} &= \left(x_{\text{Fe}}^{\text{M12}}\right)^2 \left(x_{\text{Fe}}^{\text{M3}}\right) \\a_{\text{obi}}^{\text{ideal}} &= \left(x_{\text{Mg}}^{\text{M12}}\right)^2 \left(x_{\text{Fe}}^{\text{M3}}\right)\end{aligned}$$

and the regular solution activity coefficients are

$$\begin{aligned}RT \ln \gamma_{\text{phl}} &= (1 - p_{\text{phl}})p_{\text{ann}}W_{\text{phlann}} + (1 - p_{\text{phl}})p_{\text{obi}}W_{\text{phlobi}} \\&\quad - p_{\text{ann}}p_{\text{obi}}W_{\text{annobi}} \\RT \ln \gamma_{\text{ann}} &= p_{\text{phl}}(1 - p_{\text{ann}})W_{\text{phlann}} - p_{\text{phl}}p_{\text{obi}}W_{\text{phlobi}} \\&\quad + (1 - p_{\text{ann}})p_{\text{obi}}W_{\text{annobi}} \\RT \ln \gamma_{\text{obi}} &= -p_{\text{phl}}p_{\text{ann}}W_{\text{phlann}} + p_{\text{phl}}(1 - p_{\text{obi}})W_{\text{phlobi}} \\&\quad + p_{\text{ann}}(1 - p_{\text{obi}})W_{\text{annobi}}\end{aligned}$$

For the intracrystalline reaction 2phl + ann = 3obi, whose enthalpy change is  $\Delta H_{\text{R}}^{\circ}$ , the equilibrium condition, using the expressions above, reduces to



$$0 = A + BQ + Cx + 2RT \ln K_D$$

in which

$$K_D = \frac{x_{\text{Fe}}^{\text{M3}} x_{\text{Mg}}^{\text{M12}}}{x_{\text{Fe}}^{\text{M12}} x_{\text{Mg}}^{\text{M3}}} = \frac{(1 - p_{\text{phl}})(1 - p_{\text{ann}})}{p_{\text{ann}} p_{\text{phl}}}$$

and

$$\begin{aligned} A &= \Delta H_{\text{R}}^{\circ} + 3W_{\text{phl obi}} - W_{\text{phl ann}} \\ B &= -4W_{\text{phl obi}} + \frac{4}{3}W_{\text{phl ann}} - 2W_{\text{ann obi}} \\ C &= 3W_{\text{ann obi}} - 3W_{\text{phl obi}} - W_{\text{phl ann}} \end{aligned}$$

For this first stage in deriving a mixing model for phl–ann biotite, values are required for the three interaction energies  $W_{\text{phl ann}}$ ,  $W_{\text{phl obi}}$  and  $W_{\text{ann obi}}$  and the magnitude of  $\Delta H_{\text{R}}^{\circ}$ . When the size and charge of the mixing species are very similar and the partition between the sites quite small (as they are for Fe and Mg), the cross-site terms may be insignificant, and the size of  $W_{\text{phl ann}}$  can be approximated by the sum of  $W_{\text{phl obi}}$  and  $W_{\text{ann obi}}$ . The cross-site term in orthopyroxene is negative, whereas in cummingtonite it is positive according to Holland & Powell (1996b), and so in general we might expect a zero value to be reasonable where there are no reliable experimental data. With this approximation, the three equations above simplify to  $C = 0$ ,  $A = \Delta H_{\text{R}}^{\circ}$  and  $B = -2W_{\text{ann obi}}$  (or  $B = -4W_{\text{phl obi}}$ ). Recognizing that, in the absence of significant strain energy terms,  $W_{\text{phl obi}} = W_{\text{FeMg}}^{\text{M3}}$  and  $W_{\text{ann obi}} = 2W_{\text{FeMg}}^{\text{M12}}$  allows reasonable values to be placed on all the  $W$  terms by assuming that in typical octahedral sites the value for  $W_{\text{FeMg}}$  is the same as that for olivine, around 4 kJ mol<sup>-1</sup>. Thus, to a good approximation:

$$\begin{aligned} W_{\text{phl obi}} &= 4 \text{ kJ mol}^{-1} \\ W_{\text{ann obi}} &= 8 \text{ kJ mol}^{-1} \\ W_{\text{phl ann}} &= 12 \text{ kJ mol}^{-1} \\ B &= -16 \text{ kJ mol}^{-1} \\ A &= \Delta H_{\text{R}}^{\circ} \end{aligned}$$

Therefore in simple cases of weak partitioning, all energy terms except the internal ordering reaction enthalpy can be readily approximated.  $\Delta H_{\text{R}}^{\circ}$  can be found by solving the internal equilibrium condition for a suitable value of  $Q$  at any specified temperature. For biotite it is assumed that at 700 °C the value for  $Q \approx 0.1$ , and this gives us  $\Delta H_{\text{R}}^{\circ} = -6 \text{ kJ mol}^{-1}$ . With this value,  $Q$  goes through zero and changes sign as Al content in biotite increases.

When adding octahedral Al to phl–ann biotite, an additional end-member is required, and can be chosen from either eastonite (east;  $\text{KAlMg}_2[\text{Al}_2\text{Si}_2]\text{O}_{10}(\text{OH})_2$ ) or siderophyllite (sid;  $\text{KAlFe}_2[\text{Al}_2\text{Si}_2]\text{O}_{10}(\text{OH})_2$ ). Here east is chosen, recognizing that Al–Si mixing on the T1 tetrahedral sites now is involved. The ideal part of the activity model used for this biotite involves ideal mixing on the M3, M12 and T1 sites. The site fractions are

$$\begin{aligned} x_{\text{Al}}^{\text{M3}} &= p_{\text{east}}, & x_{\text{Fe}}^{\text{M3}} &= 1 - p_{\text{east}} - p_{\text{phl}}, & x_{\text{Mg}}^{\text{M3}} &= p_{\text{phl}}, \\ x_{\text{Fe}}^{\text{M12}} &= p_{\text{ann}}, & x_{\text{Al}}^{\text{T1}} &= \frac{1 + p_{\text{east}}}{2} & \text{and } x_{\text{Si}}^{\text{T1}} &= \frac{1 - p_{\text{east}}}{2} \end{aligned}$$

and lead to the following ideal mixing activities:

$$\begin{aligned} a_{\text{phl}}^{\text{ideal}} &= 4x_{\text{Mg}}^{\text{M3}}(x_{\text{Mg}}^{\text{M12}})^2 x_{\text{Al}}^{\text{T1}} x_{\text{Si}}^{\text{T1}} \\ &= p_{\text{phl}}(1 - p_{\text{ann}})^2(1 - p_{\text{east}})(1 + p_{\text{east}}) \\ a_{\text{ann}}^{\text{ideal}} &= 4x_{\text{Fe}}^{\text{M3}}(x_{\text{Fe}}^{\text{M12}})^2 x_{\text{Al}}^{\text{T1}} x_{\text{Si}}^{\text{T1}} \\ &= (1 - p_{\text{east}} - p_{\text{phl}})p_{\text{ann}}^2(1 - p_{\text{east}})(1 + p_{\text{east}}) \\ a_{\text{east}}^{\text{ideal}} &= x_{\text{Al}}^{\text{M3}}(x_{\text{Mg}}^{\text{M12}})^2(x_{\text{Al}}^{\text{T1}})^2 \\ &= \frac{1}{4}p_{\text{east}}(1 - p_{\text{ann}})^2(1 + p_{\text{east}})^2 \\ a_{\text{obi}}^{\text{ideal}} &= 4x_{\text{Fe}}^{\text{M3}}(x_{\text{Mg}}^{\text{M12}})^2 x_{\text{Al}}^{\text{T1}} x_{\text{Si}}^{\text{T1}} \\ &= (1 - p_{\text{east}} - p_{\text{phl}})(1 - p_{\text{ann}})^2(1 - p_{\text{east}})(1 + p_{\text{east}}) \end{aligned}$$

The non-ideal contribution to the activities is provided by the symmetrical formalism (regular solution) expression for mixing among the independent end-member set phl–ann–obi–east. Interaction energies for the three extra parameters relating east to phl, ann and obi ( $W_{\text{phl east}}$ ,  $W_{\text{ann east}}$  and  $W_{\text{obi east}}$ ) need to be found to complete the mixing model for aluminous biotite. The calorimetric data of Circone & Navrotsky (1992) on the phl–east join can be taken to imply  $W_{\text{phl east}}$  is around  $10 \pm 4 \text{ kJ mol}^{-1}$ , if the most discrepant calorimetric measurement is discarded, following the reasoning in Holland & Powell (1998). To get the last two terms requires the help of the dependent end-member relations (conveniently done by the *depem* function provided in Powell & Holland, 1999) among the chosen independent set of end-members and the end-member sid:

$$\begin{aligned} W_{\text{phl sid}} &= W_{\text{phl ann}} + W_{\text{phl east}} - W_{\text{phl obi}} - W_{\text{ann east}} \\ &\quad + W_{\text{ann obi}} + W_{\text{east obi}} \\ W_{\text{ann sid}} &= W_{\text{east obi}} \\ W_{\text{sid obi}} &= -W_{\text{ann east}} + 2W_{\text{ann obi}} + 2W_{\text{east obi}} \end{aligned}$$

From the second of these we can determine  $W_{\text{east obi}}$  if a value for  $W_{\text{ann sid}}$  is known. Several others, e.g. Indares & Martignole (1985), McMullin *et al.* (1991) and Holdaway (2000) have argued from natural assemblages that the value for  $W_{\text{FeAl}}$  is somewhat smaller than  $W_{\text{MgAl}}$ . Although all these authors used a disordered model involving phlogopite, annite and a hypothetical biotite with three octahedral Al, their conclusions with regard to the effect of Al on the garnet–biotite thermometer remain valid. Their interaction energies cannot be readily cast in terms of phl–east and ann–sid, because their assumption was one of complete disorder over three sites, and because the energetics of Mg–Al ordering in phlogopite are unknown. There is also considerable debate (e.g. in Holdaway, 2000) on the effects of ferric iron on biotite energetics, and the numerical values for derived  $W_{\text{MgAl}}$



and  $W_{\text{FeAl}}$  show much scatter. Nevertheless, their analysis suggests a proportionately smaller value for  $W_{\text{ann sid}}$  than  $W_{\text{phl east}}$  and so  $W_{\text{ann sid}}$  (and hence also  $W_{\text{east obi}}$ ) is taken to be  $7 \text{ kJ mol}^{-1}$ . The only parameter remaining to be calibrated is  $W_{\text{ann east}}$ ; assuming that the difference between the experimental values of Ferry & Spear (1978) and Perchuk & Lavrent'eva (1983) for  $\log K_D$  for biotite and garnet are largely due to more aluminous biotite in the latter (see Powell & Holland, 1999, Fig. 7),  $W_{\text{ann east}} = 3 \text{ kJ mol}^{-1}$  is set to complete the model, giving the final set of parameters for biotite as:

$$\begin{aligned}W_{\text{phl obi}} &= 4 \text{ kJ mol}^{-1} \\W_{\text{ann obi}} &= 8 \text{ kJ mol}^{-1} \\W_{\text{phl ann}} &= 12 \text{ kJ mol}^{-1} \\W_{\text{phl east}} &= 10 \text{ kJ mol}^{-1} \\W_{\text{ann east}} &= 3 \text{ kJ mol}^{-1} \\W_{\text{obi east}} &= 7 \text{ kJ mol}^{-1} \\ \Delta H_{\text{R}}^{\circ} &= -6 \text{ kJ mol}^{-1}\end{aligned}$$

This model is an improvement in two respects over the model outlined as an example in Powell & Holland (1999): first, the interaction energies for individual octahedra have been raised from 3 to  $4 \text{ kJ mol}^{-1}$  to be more like those in olivine, and second, the degree of ordering has been reduced. This latter point is important because the M1, M2 and M3 octahedra in biotite are quite similar and site partition of Fe and Mg is quite weak (Brigatti *et al.*, 2000). Furthermore, the partitioning can be made to reverse with Al occupancy if the value for  $\Delta H_{\text{R}}^{\circ}$  is made much smaller than assumed in Powell & Holland (1999). This model will require future refinement and extension to include the effects of Ti and  $\text{Fe}^{3+}$  as well as possible differences between octahedral and tetrahedral Al contents, using substitutions more complex than simple tschermak exchange. This example nevertheless serves to illustrate how activity-composition models for minerals may be derived from quite simple assumptions without invoking equipartition.

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