

# Modelling excess properties of mineral and melt solutions over large P-T ranges: implications for phase relations and seismic velocities in the mantle

R. Myhill

*Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany*

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## Abstract

Thermodynamic models of solid and liquid solutions in the Earth Sciences are increasingly used to calculate phase relations and seismic properties over large pressure and temperature ranges. Calculations often span over 1000 K and 5 GPa in studies of exhumation processes and metamorphism in subduction zones. Research into mantle phase relations and differentiation of the early Earth frequently involves calculations over 3000 K and 100 GPa. Despite spanning such huge ranges, a common approximation is that excess thermodynamic derivatives within solid solutions (entropy and volume) are pressure-temperature invariant. If these excesses are large, the approximation can result in large errors in gibbs free energy at high pressure and temperature, and errors in seismic velocities even within the range of calibration conditions.

In this paper, we present a solution to this problem by extending the sub-regular Margules mixing model using intermediate compounds to define the thermodynamic properties of solid solutions. Mathematical derivations are provided for excess properties ( $H^{ex}$ ,  $S^{ex}$ ,  $V^{ex}$ ) and their pressure and temperature derivatives ( $K_T^{ex}$ ,  $\alpha^{ex}$ ,  $Cp^{ex}$  etc.). We provide examples of pyroxene, garnet and melt solutions, showing that inclusion of a variable excess volume is vital to simulate observed phase relations and seismic velocities. Heuristics are sug-

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\*Corresponding author: R. Myhill  
Email address: [myhill.bob@gmail.com](mailto:myhill.bob@gmail.com) (R. Myhill)

gested for intermediate compounds where individual thermodynamic properties are poorly constrained.

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## 1. Introduction

Thermodynamic models of solid and liquid solutions in the Earth Sciences are an integral part of

The approximation of constant positive excess volume implicitly yields an  
5 excess positive bulk modulus and negative thermal expansion, in conflict with  
both intuition and experimental observations. This is a particular problem  
where thermodynamic data are used over pressure ranges exceeding a few GPa,  
and where they are used to compute seismic wave velocities.

In many circumstances, these shortcomings are unimportant. However, there  
10 is a fundamental need to adjust the solid solution model where the stability range  
of the solid solution extends over pressure regimes large enough to contribute  
significantly to changes in excess enthalpy inconsistent with data, or mineral  
phases exhibit significant excess bulk moduli. The latter is especially important  
for those studies where velocities are obtained from the models.

15 The models in this study are all implemented in the open software *burnman*,  
a mineral physics toolkit written in python. The software, first described in  
Cottaar et al. (2014), was originally designed for seismic velocity calculations.  
It has since been augmented with thermodynamics functionality, including a  
range of different models for solid solutions.

## 20 2. The Extended Subregular Margules (ESM) model

The subregular Margules mixing model within a binary system approximates  
excess Gibbs free energies at any given pressure and temperature as a cubic  
function of composition (Helffrich and Wood, 1989):

$$\mathcal{G}^{xs} = W_{12}X_1X_2^2 + W_{21}X_1^2X_2 \quad (1)$$

The terms  $W_{ij}$  describing the interaction between endmembers  $i$  and  $j$  are  
 25 normally described by a function of the form

$$W_{ij} = a_{ij} + b_{ij}P + c_{ij}T \quad (2)$$

dropbox In the ESM model, we instead define properties for each binary pair  
 based on two intermediate compounds with compositions  $X_i = X_j = 0.5$ . For  
 the special case of a symmetric mixing model, the properties for both interme-  
 diates are the properties of a compound with that composition; otherwise, both  
 30 compounds are fictional. The interaction terms are now defined as:

$$W_{ij}^{\mathcal{G}} = 4(\mathcal{G}_{ij} + T\mathcal{S}_{ij}^{\text{conf}}) - 2(\mathcal{G}_i + \mathcal{G}_j) \quad (3)$$

where  $\mathcal{S}_{ij}^{\text{conf}}$  is the configurational entropy of the intermediate compound, which  
 depends on the number of sites on which mixing occurs. For a solution with  $n$   
 independent endmembers, and ignoring ternary terms, the excess nonconfigura-  
 tional Gibbs free energy is (Helffrich and Wood, 1989)

$$\mathcal{G}^{xs} = \sum_{i=1}^n \sum_{j>1}^n X_i X_j \left( W_{ij} X_j + W_{ji} X_i + 0.5(W_{ij} + W_{ji}) \sum_k^n (1 - \delta_{ik})(1 - \delta_{jk}) X_k \right) \quad (4)$$

35 Using this new model, we can now define the properties of the solid solution  
 as follows:

$$\mathcal{G} = \sum_i X_i \mathcal{G}_i + \mathcal{G}^{xs} \quad (5)$$

$$\mathcal{H} = \sum_i X_i \mathcal{H}_i + \mathcal{H}^{xs} \quad (6)$$

$$\mathcal{S} = \sum_i X_i \mathcal{S}_i + \mathcal{S}^{xs} \quad (7)$$

$$\mathcal{V} = \sum_i X_i \mathcal{V}_i + \mathcal{V}^{xs} \quad (8)$$

$$C_P = \sum_i X_i C_P + T \left( \frac{\partial \mathcal{S}}{\partial T} \right)_P^{xs} \quad (9)$$

$$\alpha = \frac{1}{\mathcal{V}} \left( \sum_i X_i \alpha_i \mathcal{V}_i + \left( \frac{\partial \mathcal{V}}{\partial T} \right)_P^{xs} \right) \quad (10)$$

$$K_T = \frac{\mathcal{V}}{\sum_i \frac{X_i \mathcal{V}_i}{K_{Ti}} - \left( \frac{\partial \mathcal{V}}{\partial P} \right)_T^{xs}} \quad (11)$$

$$C_V = C_P - \mathcal{V} T \alpha^2 K_T \quad (12)$$

$$K_S = K_T \frac{C_P}{C_V} \quad (13)$$

$$\gamma = \frac{\alpha K_T \mathcal{V}}{C_V} \quad (14)$$

With the exception of the enthalpy excess, excess terms ( $\mathcal{S}^{xs}$ ,  $\mathcal{V}^{xs}$  etc) are derived in the same way as the excess Gibbs free energy (Equation 4), with interaction terms defined as follows:

$$W_{ij}^{\mathcal{S}} = 4(\mathcal{S}_{ij} - \mathcal{S}_{ij}^{\text{conf}}) - 2(\mathcal{S}_i + \mathcal{S}_j) \quad (15)$$

$$W_{ij}^{\mathcal{V}} = 4\mathcal{V}_{ij} - 2(\mathcal{V}_i + \mathcal{V}_j) \quad (16)$$

$$W_{ij}^{\partial \mathcal{V} / \partial P} = -4\mathcal{V}_{ij} / K_{Tij} + 2(\mathcal{V}_i / K_{Ti} + \mathcal{V}_j / K_{Tj}) \quad (17)$$

$$W_{ij}^{\partial \mathcal{V} / \partial T} = 4\alpha_{ij} \mathcal{V}_{ij} - 2(\alpha_i \mathcal{V}_i + \alpha_j \mathcal{V}_j) \quad (18)$$

$$W_{ij}^{\partial \mathcal{S} / \partial T} = \frac{4C_{Pij} - 2(C_{Pi} + C_{Pj})}{T} \quad (19)$$

40 Finally, excess enthalpy is defined as

$$\mathcal{H}^{xs} = \mathcal{G}^{xs} + T\mathcal{S}^{xs} \quad (20)$$

### 2.1. Heuristics

It is often the case that endmembers are particularly well studied, while the properties of the solid solution are constrained only by enthalpies of solution and volumes at room temperature and pressure. In the absence of other data, heuristics are required to constrain the properties of the intermediate compounds. In  
45 this study, we suggest that the following heuristics be used:

$$\mathcal{S}_{ij} = 0.5(\mathcal{S}_i + \mathcal{S}_j) + \mathcal{S}_{ij}^{\text{conf}} \quad (21)$$

$$C_{Pij} = 0.5(C_{Pi} + C_{Pj}) \quad (22)$$

$$\alpha_{ij} = 0.5\mathcal{V} \left( \frac{\alpha_i}{\mathcal{V}_i} + \frac{\alpha_j}{\mathcal{V}_j} \right) \quad (23)$$

$$K'_T = -\frac{\partial}{\partial P} \left( \mathcal{V} \left( \frac{\partial P}{\partial \mathcal{V}} \right)_T \right) \sim \mathcal{V} \left( \sum_i \frac{X_i \mathcal{V}_i}{K'_{Ti} + 1} \right)^{-1} - 1 \quad (24)$$

If excess volumes are zero, the bulk modulus is given by Equation 11, with the differential term equal to zero. However, non-zero excess volumes are unlikely to remain constant with pressure and temperature. Mixing of elements with different ionic radii and chemical bonding on sites affects not only the packing efficiency, but also the mechanisms of compression. A positive excess volume implies a more open structure which will be more prone to volume decrease on compression.

We suggest that, in the absence of other data it should be assumed that  $\left( \frac{\partial \mathcal{V}}{\partial P} \right)_T^{xs} \rightarrow 0$  as  $P \rightarrow \infty$ . Bulk moduli for intermediates can then be constrained.

$$K_T \sim 0.5(K_{Ti} + K_{Tj}) + c \left( \frac{K_{Ti}\mathcal{V}_j + K_{Tj}\mathcal{V}_i}{\mathcal{V}_i + \mathcal{V}_j} - 0.5(K_{Ti} + K_{Tj}) \right) \quad (25)$$

The factor  $c$  before the second term on the RHS of Equation 25 modifies the rule of thumb proposed by Anderson and Anderson (1970) to estimate the compressibility of endmembers based on their molar volumes. Typically, values of  $c$  from 4 to 12 satisfy our proposed heuristic.

### 3. Examples

#### 3.1. Pyroxene

Our first example is that of jadeite-aegirine pyroxene, an almost ideal solid solution (from a volumetric perspective). We use this model to illustrate that even when excess volumes are extremely small, excess bulk moduli are resolvable. The experimental data is that of Nestola et al. (2006), and the equation of state used is the Modified Tait (Holland and Powell, 2011). The fit to the volume data is shown in Figure 1.

Using the derived properties of the solid solution, we can fit the excess volume as a function of pressure (Figure 2). The decay of excess volume as a function

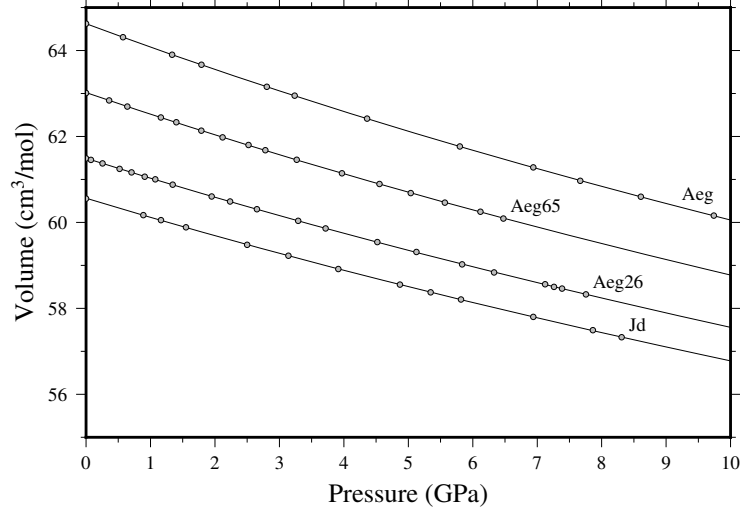


Figure 1: Pressure-volume data in the binary system Jadeite-Aegirine (Nestola et al., 2006), with the model proposed in this study.

Table 1: Jadeite-Aegirine mixing parameters to fit the room temperature data of Nestola et al. (2006). The value for  $K'_0$  is fixed to the value given by the heuristic proposed in the text.  $K''_0 = -K'_0/K_0$ .

	jadeite	aegirine	jd50ae50	ae50jd50
$V_0$ (cm <sup>3</sup> /mol)	$60.5640 \pm 0.0001$	$64.6261 \pm 0.0004$	$62.3641 \pm 0.0005$	$62.4522 \pm 0.0005$
$K_0$ (GPa)	$133.5 \pm 0.2$	$116.0 \pm 0.2$	$124.8 \pm 0.5$	$126.7 \pm 0.4$
$K'_0$	4.6	4.4	4.4785	4.4785

of pressure is in excellent agreement with the heuristic proposed in the previous section.

### 3.2. Garnet

Our second example is the pyrope-grossular join, which is well-known to have significant non-ideality and volumes of mixing. Here we use the excess volume of Du et al. (2015), approximating the solid solution as symmetric and using the heuristics described above.

P-wave , S-wave and bulk sound velocities are functions of isentropic bulk

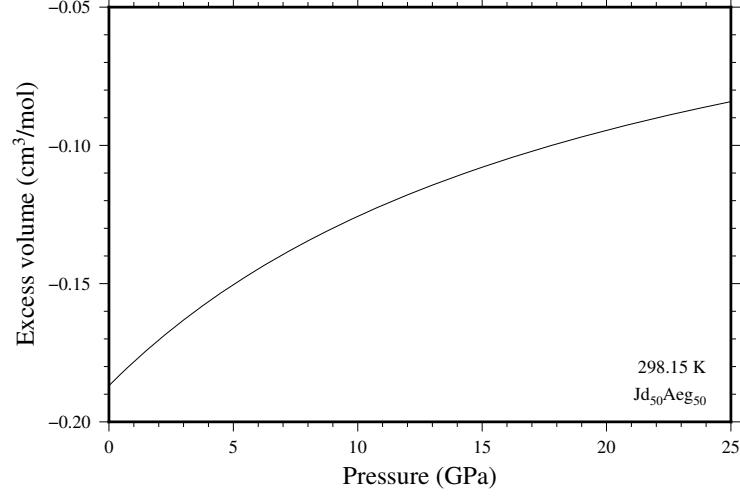


Figure 2: Excess volume for  $\text{Jd}_{50}\text{Aeg}_{50}$  calculated from our model.

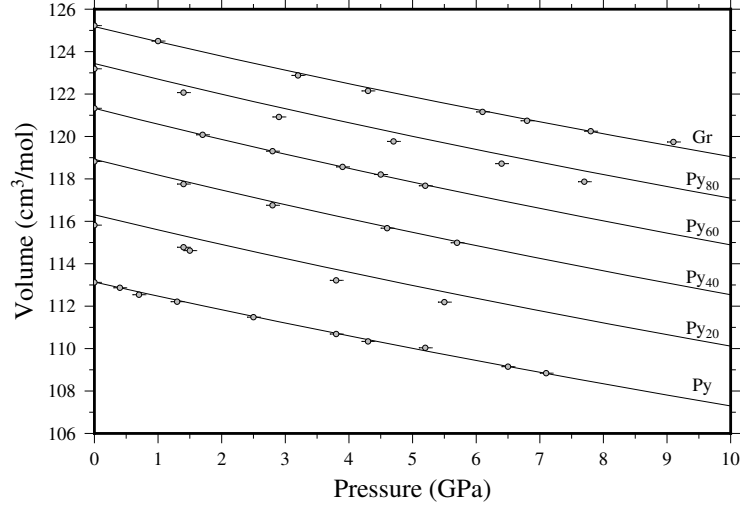


Figure 3: Pressure-volume data in the binary system Pyrope-Grossular (Du et al., 2015), with the model proposed in this study.

and shear moduli and density:

$$V_P = \sqrt{\frac{K_S + \frac{4}{3}G}{\rho}} \quad (26)$$

$$V_S = \sqrt{\frac{G}{\rho}} \quad (27)$$

$$V_\Phi = \sqrt{\frac{K_S}{\rho}} \quad (28)$$

To illustrate the effect of excess bulk moduli on seismic wave velocities, we  
 80 plot  $V_\Phi$  for a 50:50 molar mix of pyrope and grossular according to three solid  
 solution models (Figure 4).

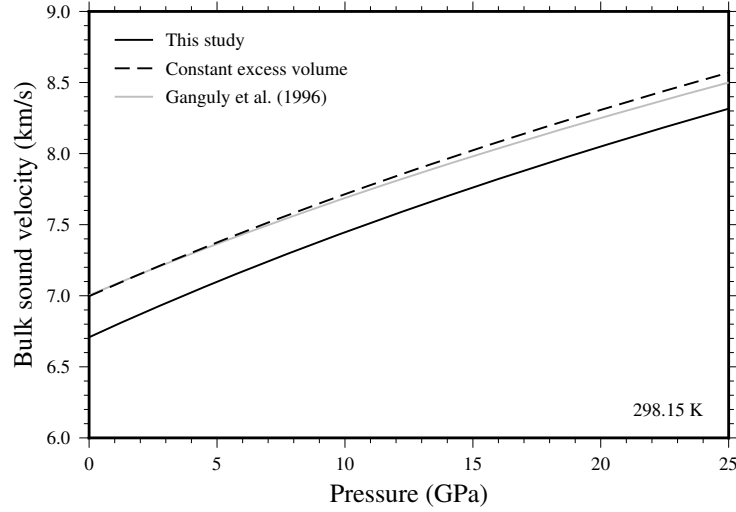


Figure 4: Bulk sound velocities of  $\text{Py}_{50}\text{Gr}_{50}$  at room temperature according to the model of (Ganguly et al., 1996), a fixed excess volume based on room pressure data (Du et al., 2015) and a full subregular model incorporating excess bulk moduli, from the same study.

We note that for natural garnet,  $(\partial \ln V_S / \partial \ln V_P)_P \sim 1$  (Chai et al., 1997), and therefore  $V_P/V_S \sim c$  with varying temperature. With this in mind,  $V_P$  and  $V_S$  should be constant fractions of the bulk sound velocity  $V_\Phi$ .

### 85 3.3. Fe-O melt

Our final example is that of Fe-FeO melt. This liquid solution is extremely important for understanding partitioning of oxygen into the Earth's core. At pressures  $< 25$  GPa, the solution exhibits significant non-ideality, with a large miscibility gap between ionic and metallic Fe-O liquids (Frost et al., 2010). As



90 pressure increases, this miscibility gap disappears, indicating a negative excess  
volume of mixing (Figure 5). Komabayashi (2014) uses an ideal model at high  
pressure, and obtains a more-or-less reasonable fit to the available experimental  
data.

To model processes of mantle differentiation and core formation, it would be  
95 extremely useful to have a single model describing the properties of melts over  
relevant pressure and temperature ranges. Clearly a high pressure ideal model  
cannot be reconciled with a low pressure model with large excess volumes of  
mixing without incorporating excess bulk moduli and thermal expansivities.  
Here, we use the compositions of coexisting metallic and ionic liquid ( ) and the  
100 pressure, temperature and compositions of eutectic liquid at high pressure ( )  
to constrain the mixing properties of Fe-FeO liquid (Figure 6). The eutectic  
temperature and composition above 25 GPa are shown in Figure 7.

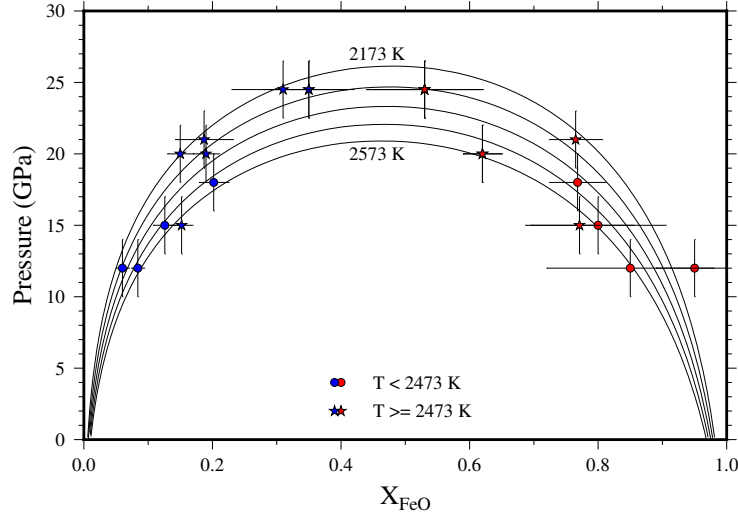


Figure 5: Fe-O solvus

#### 4. Conclusions

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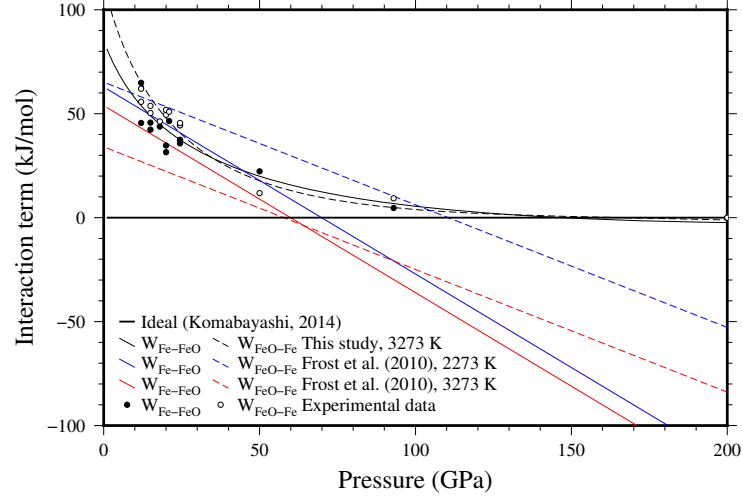


Figure 6: Interaction terms in Fe-FeO melt as a function of pressure.

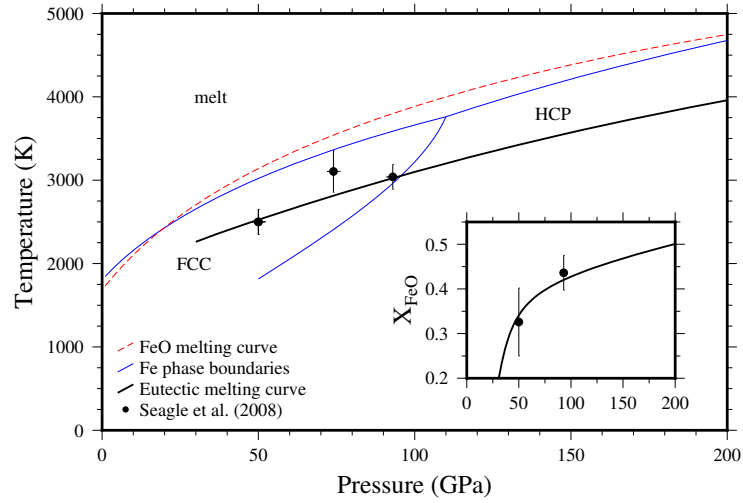


Figure 7: Melting temperature in the Fe-O system as a function of pressure. Inset: eutectic composition in the Fe-O system.

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