

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

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

*Keywords:* high pressure, excess properties

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## 1. Introduction

Solution models are a vital part of estimating phase relations in the Earth. Typically, some functional form (often quadratic, cubic) is used to describe excess non-configurational energies between endmembers. Where necessary, the  
5 parameters describing the properties of the solid solution are allowed to vary as a function of pressure and temperature.

$$W_{ij} = W_{ij}^H + W_{ij}^V P + W_{ij}^S T \quad (1)$$

Models described in this way have been extremely successful in describing the properties of solid solutions up to pressures of a few GPa. Increasingly, such models are being used over larger and larger pressure ranges. For example,  
10 garnet models are now being used to estimate phase relations in the mantle transition zone, and models of metallic alloys and melts are being used to study the composition and evolution of the Earth's core. Another development is the increasing use of solution models to estimate seismic velocities in the mantle and core. These two developments present a problem for the traditional approach  
15 described in Equation 1, because they are both strongly dependent on the change in excess volume with pressure, a variable which is generally not zero.

We introduce here a simple adaptation of mixing models, which use intermediate compounds to describe the excess properties of the solid solution as a function of pressure and temperature. With this added flexibility comes a large  
20 increase in the number of free parameters, so we also provide useful heuristics for the cases where individual parameters are unknown.

The new form of the model is illustrated with the use of three implementations for pyroxene, garnet and Fe-FeO melt. We show that for these cases: a constant excess volume based on room pressure data is a bad approximation

25 beyond a few GPa pressure, and major errors in seismic velocities and phase relations result from not incorporating reasonable decays in excess volume. 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  
 30 since been augmented with thermodynamics functionality, including a range of different models for solid solutions.

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

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

$$\mathcal{G}^{xs} = X_B(1 - X_B)(W_{AB}X_B + W_{BA}(1 - X_B)) \quad (2)$$

In the special case that  $W_{AB} = W_{BA}$ , the function is a quadratic. We can define the Gibbs interaction parameter in terms of the Gibbs free energy of a 50:50 intermediate compound ( $AB$ ) and the endmembers  $A$  and  $B$ :

$$W_{AB}^{\mathcal{G}} = 4(\mathcal{G}_{AB} + T\mathcal{S}_{AB}^{\text{conf}}) - 2(\mathcal{G}_A + \mathcal{G}_B) \quad (3)$$

where  $\mathcal{S}_{AB}^{\text{conf}}$  is the configurational entropy of the intermediate compound. In  
 40 the more general case that  $W_{AB} \neq W_{BA}$ , Equation 2 can be thought of as two symmetric interaction parameters with contributions that depend on the composition. Two intermediate compounds ( $AB$  and  $BA$ ) are then required to describe the properties of the solution (Figure 1).

Expanding the subregular solution model beyond a binary system, the excess  
 45 nonconfigurational Gibbs free energy is (Helffrich and Wood, 1989)

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

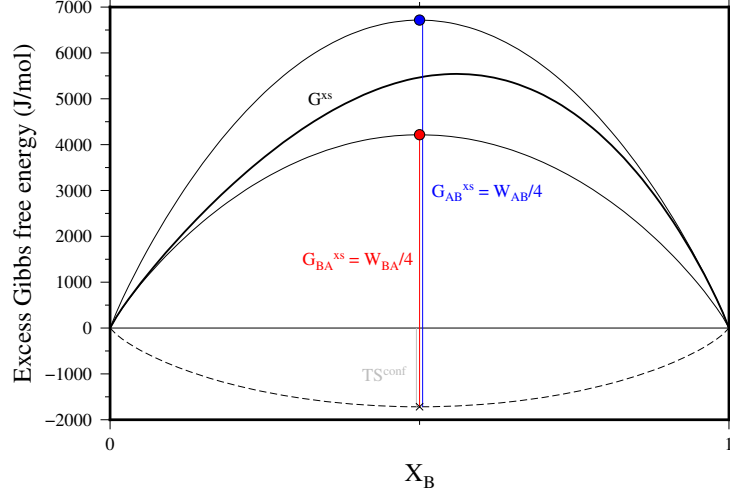


Figure 1: Schematic illustration of a binary subregular solution model.

Each of the individual  $W_{ij}$  terms in Equation 4 can be determined via the properties of an intermediate compound, just as described in the binary  $A$ - $B$  system (Equation 2). The properties of the solid solution with composition  $X_i$  are then defined as follows:

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

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

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

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

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

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

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

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

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

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

50 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:

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

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

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

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

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

Finally, excess enthalpy is defined as

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

### 2.1. Heuristics

55 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. The remaining properties of the intermediate compounds must be estimated by the user. In this study, we suggest that the following heuristics be used:

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

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

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

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

60 If excess volumes are zero, it is likely that they will remain zero as temperatures and pressures increase. In this case, the bulk modulus is given by

Equation 11, with the differential term equal to zero. In contrast, non-zero excess volumes are unlikely to remain constant with pressure and temperature. Mixing of elements with different ionic radii and field strengths result in lattice distortions, and a series of weaker or stronger bonds. It is reasonable to assume that a positive volume excess results in longer bonds which are, on average, more compressible, and that a negative volume excess results in reduced compressibility. In this case, a positive volume excess results in a negative excess bulk modulus. We suggest that, in the absence of other data a useful heuristic is the suggestion that  $\left(\frac{\partial \mathcal{V}}{\partial P}\right)_T^{xs} \rightarrow 0$  as  $P \rightarrow \infty$ .

A useful way to view the change in bulk modulus across a solid solution is to compare the excess bulk modulus to that implied by the  $K_T V = \text{constant}$  rule of thumb proposed by Anderson and Anderson (1970) to estimate the compressibility of endmembers based on their molar volumes. The heuristic we propose in this study predicts a larger excess term than that suggested by the rule of thumb, which we describe using a factor  $\xi$ :

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

Typically, a value of  $\sim 6$  provides a useful estimate of  $\xi$ .

Now that we have described the new model, we turn to a few geologically relevant examples.

### 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 2.

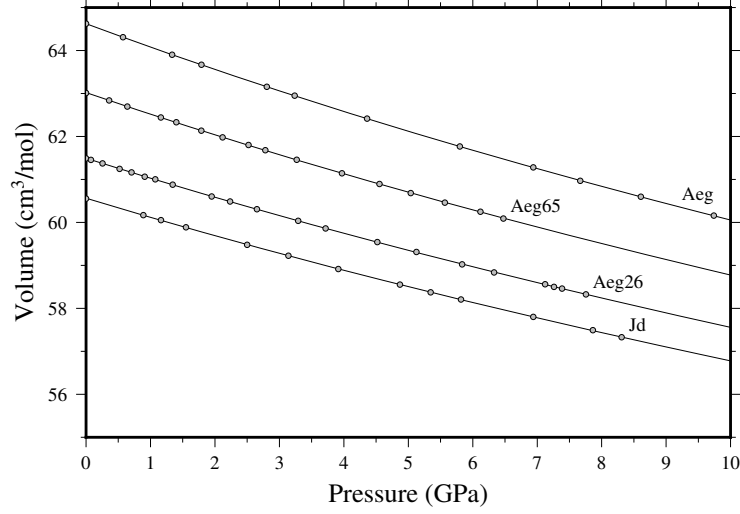


Figure 2: Pressure-volume data in the binary system Jadeite-Aegirine (Nestola et al., 2006), with the model proposed in this study.

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

	jadeite	aegirine	jd <sub>50</sub> ae <sub>50</sub>	ae <sub>50</sub> jd <sub>50</sub>
$V_0$ (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 [fixed]	4.4 [fixed]	4.4785 [heuristic]	4.4785 [fixed]

Using the derived properties of the solid solution, we can fit the excess volume as a function of pressure (Figure 3). The decay of excess volume as a function  
90 of pressure is in excellent agreement with the prediction that excess volumes decay to zero at extreme pressures. For the 50:50 intermediate, the Equation 25 is satisfied when  $\xi \sim 10$ .

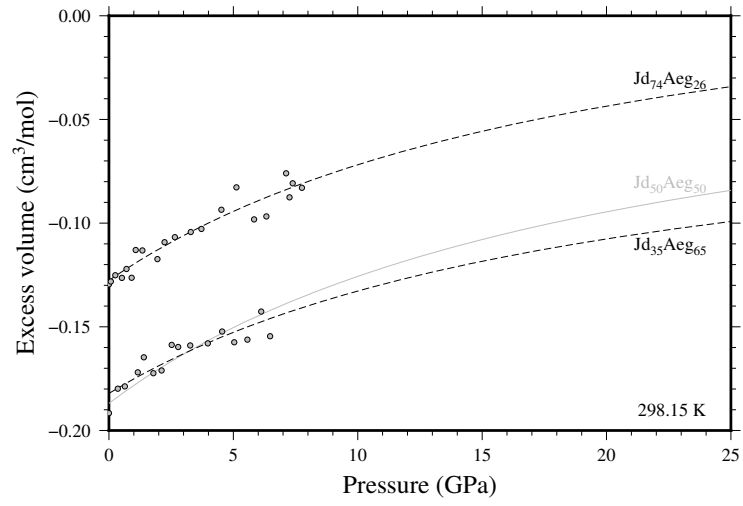


Figure 3: Excess volume for Jd-Aeg pyroxenes calculated from our model.



### 3.2. Garnet

Our second example is the pyrope-grossular join, which is well-known to have  
95 significant non-ideality and volumes of mixing (Newton et al., 1977; Bosenick  
and Geiger, 1997; Ganguly et al., 1996). Recently, it has been suggested that  
the excess volumes of mixing are  $\sim 1 \text{ cm}^3/\text{mol}$ , 2–3 times larger than previously  
suggested, and associated with very large negative excess bulk moduli (Du et al.,  
2015). If this were true, it would have significant implications for phase relations  
100 and seismic velocities in the mantle.

Here, we create four models to describe the room temperature equations of  
state for the pyrope-grossular system. Two models are presented for the data  
of (Du et al., 2015), to describe the reported behaviour close to the center and  
at the edges of the solid solution. The third model is the constant volume  
105 subregular Margules model of Ganguly et al. (1996). A fourth model has the  
same excess volume as Ganguly et al. (1996), but a negative excess bulk modulus  
which allows the excess volume to decay to zero at high pressures. The standard  
state bulk moduli are shown in Figure 4.

Table 2: Pyrope-Grossular mixing parameters to fit the P-V-T data of Du et al. (2015). The  
 $K'_0$  for the ordered intermediate compound is fixed to the value given by the heuristic proposed  
in the text. The extreme  $K_0$  and  $K'_0$  for the disordered intermediate compound are required  
to avoid negative volume excesses at high pressure.  $K''_0 = -aK'_0/K_0$ , where  $a = 1$  and  $a = 52$   
for the ordered and disordered compounds respectively.

	pyrope	grossular	py <sub>50</sub> gr <sub>50</sub> (ord)	py <sub>50</sub> gr <sub>50</sub> (disord)
$V_0 \text{ (cm}^3/\text{mol)}$	$113.14 \pm 0.02$	$125.18 \pm 0.03$	$120.13 \pm 0.03$	$119.63 \pm 0.06$
$K_0 \text{ (GPa)}$	$168 \pm 2$	$173 \pm 2$	$159 \pm 3$	127 [see caption]
$K'_0$	4.4 [fixed]	5.5 [fixed]	4.975 [heuristic]	22 [see caption]
$\alpha_0 \text{ (10}^{-5}/\text{K)}$	$2.58 \pm 0.06$	$2.15 \pm 0.05$	$2.12 \pm 0.07$	$1.88 \pm 0.16$

Figure 4: Bulk moduli in the binary system Pyrope-Grossular (Du et al., 2015), with the  
models proposed in this study.

XXXX Discussion

110 These models are now used to illustrate the effect of decaying excess vol-  
 umes on seismic wave velocities. P-wave, S-wave and bulk sound velocities are  
 functions of isentropic bulk and shear moduli and density:

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

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

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

Thermodynamic solution models say nothing about shear moduli, so we restrict  
 our discussion to the bulk sound velocity. Figure 5 shows the bulk sound velocity  
 115 at ambient temperature for the four solid solution models in the text. XXXX  
 Discussion

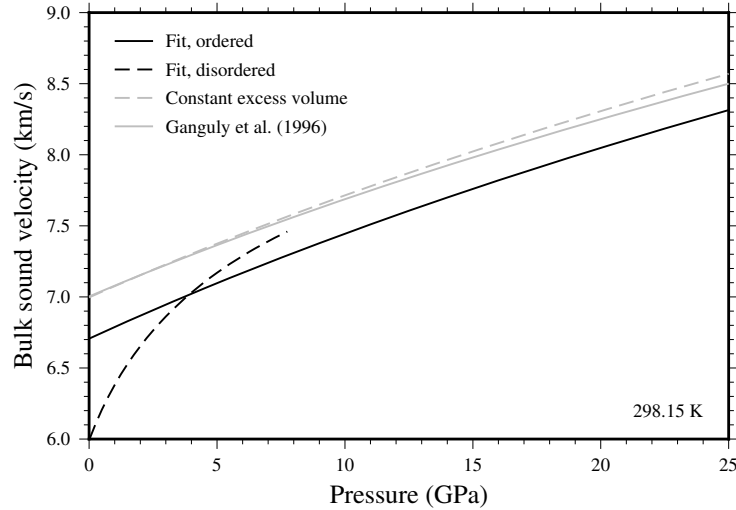


Figure 5: Bulk sound velocities of  $\text{Py}_{50}\text{Gr}_{50}$  at room temperature according to the model of (Ganguly et al., 1996), a fixed excess volume based on room pressure data (Du et al., 2015) and the two full subregular models incorporating excess bulk moduli introduced in the present study.

### 3.3. Fe-FeO melt

Our final example is that of Fe-FeO melt. As oxygen may be one of the more abundant light elements in the core, understanding the thermodynamics of this liquid solution is an important part of understanding mantle-core differentiation and interaction over billions of years. At pressures  $<25$  GPa, the Fe-FeO solution exhibits significant non-ideality, with a large miscibility gap between ionic and metallic Fe-O liquids (Kowalski and Spencer, 1995; Tsuno et al., 2007; Frost et al., 2010). As pressure increases, this miscibility gap disappears, indicating a negative excess volume of mixing (Figure 6). To explain the increase in eutectic temperature with pressure, Komabayashi (2014) suggest that mixing becomes essentially ideal at  $>100$  GPa.

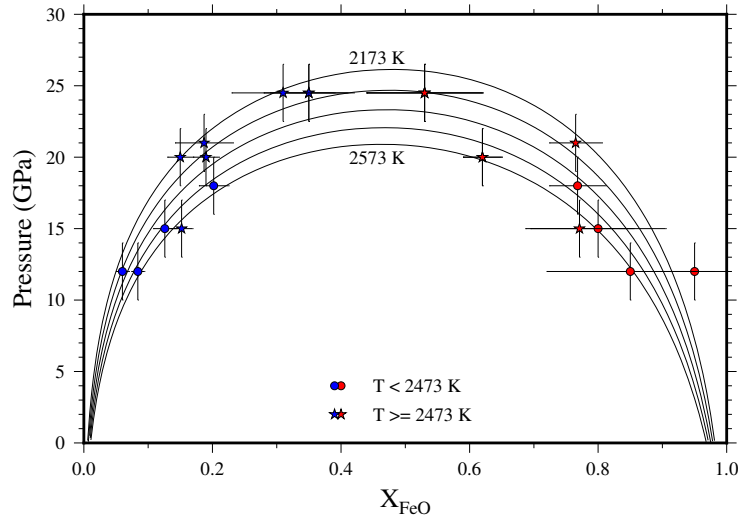


Figure 6: Fe-O solvus

To model processes of mantle differentiation and core formation, it would be 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. Below  $\sim 25$  GPa, the properties of the liquid can be estimated using the compositions

of coexisting metallic and ionic liquid (Tsuno et al., 2007; Frost et al., 2010).

135 The chemical potentials of Fe and FeO are equal in the ionic and metallic liquids, providing the two constraints necessary to estimate Margules parameters at each pressure and temperature (Figure 7).

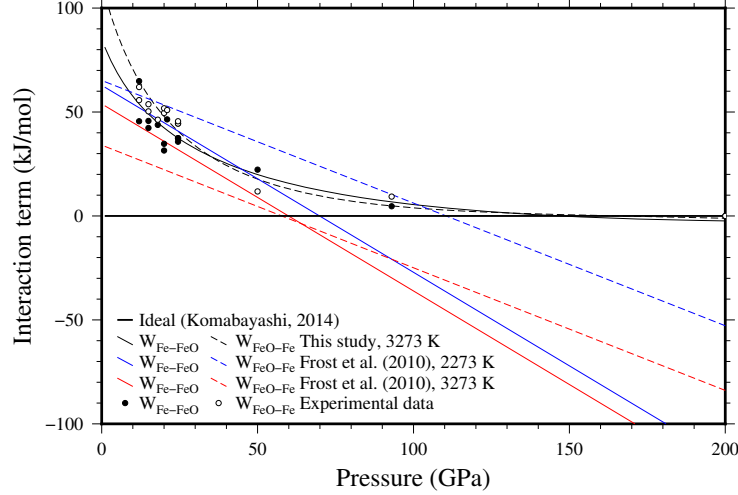


Figure 7: Interaction terms in Fe-FeO melt as a function of pressure.

At  $>25$  GPa, the pressure, temperature and compositions of eutectic liquid at high pressure (Seagle et al., 2008) provide further constraints, providing we know the relative gibbs free energies of liquid and solid Fe and FeO. Here, we fit the thermodynamic properties of the FCC and HCP iron endmembers and of B1 FeO to published P-V-T data and phase boundaries. The liquid endmembers are fit with available room pressure data, and the effect of pressure is estimated using constraints on the melting curves from Anzellini et al. (2013), Seagle et al. (2008) and Ozawa et al. (2011). The uncertainties on composition and temperature of the eutectic are rather large, so these data are supplemented by the requirement that excess volumes become zero at very high pressure. The parameters used to create the fits in Figures 7 and 8 are given in Table 3. In this work, we fix excess entropy and thermal expansion to zero. The majority of the  $<25$  GPa data was collected within a  $\sim 200$  K temperature range, and is associated with similar temperature uncertainties, which introduces very large uncertainties in

excess entropies. Add to that the possibility of phase separation during quench and the large uncertainty in coexisting ionic/metallic melt compositions, there is no clear evidence for the large temperature dependence proposed by Frost  
 155 et al. (2010), although they do slightly improve the fit to the data (mostly by increasing the pressure at which the solvus closes at high temperature).

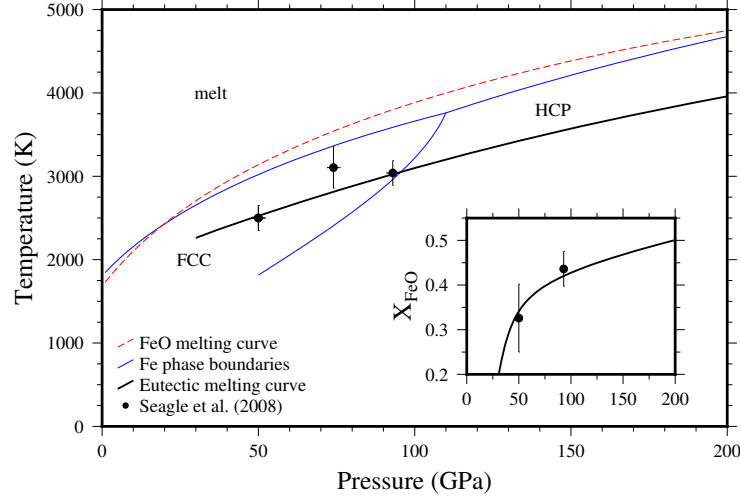


Figure 8: Melting temperature in the Fe-O system as a function of pressure. Inset: eutectic composition in the Fe-O system.

Table 3: Excess Fe-FeO mixing parameters to fit the data in Figures 7 and 8 at a reference temperature of 1809 K and pressure of 50 GPa.

Property	Fe <sub>50</sub> FeO <sub>50</sub>	FeO <sub>50</sub> Fe <sub>50</sub>
$H^{xs}$ (J/mol)	$5000 \pm 400$	$4400 \pm 400$
$S^{xs}$ (J/K/mol)	0 [fixed]	0 [fixed]
$V^{xs}$ (cm <sup>3</sup> /mol)	$-0.117 \pm 0.009$	$-0.136 \pm 0.009$
$K^{xs}$ (GPa)	$28 \pm 5$	$45 \pm 5$
$K'^{xs}$	$-0.07 \pm 0.12$	$-0.37 \pm 0.12$
$a^{xs}$	0 [fixed]	0 [fixed]

## 4. Discussion

The use of intermediate compounds to describe excess properties is an extremely simple but powerful concept that lends a great deal of flexibility to models without necessarily increasing the number of parameters which need to be fit to the available experimental data. We note that the equations derived here are all quite general, and therefore easily applicable to a wide range of different equations of state.

The heuristics suggested here place constraints on seismic properties which are significantly more strict than typical uncertainties on bulk moduli derived from ultrasonic interferometry, Brillouin scattering or static compression. For example, along the pyrope-majorite join, excess volumes are small ( $0.1 \text{ cm}^3/\text{mol}$ ) (Heinemann et al., 1997). With the assumption that excess volumes decrease to zero with increasing pressure, the excess bulk modulus is constrained to be  $\sim 0.6$  GPa. In comparison, the range in bulk modulus estimates anywhere along the pyrope-majorite join is about 10 GPa (see, for example ?). So far, high pressure elasticity studies have mostly been focussed on binary joins with small excess volumes at ambient pressure (Fan et al., 2015; Huang and Chen, 2014). That they should small excess bulk moduli is in good agreement with the heuristics proposed here, but a far more rigorous test would be to investigate systems with large volume excesses.

It is envisaged that the model formulation proposed in this study will be very useful in modelling silicate and metallic melts, where excess volumes are large at low pressure. Even in the  $\text{MgO-SiO}_2$  system, excess entropies and volumes are strongly dependent on temperature and pressure (de Koker et al., 2013).

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