A revised model for activity–composition relations in solid and molten FePt alloys and a preliminary model for characterization of oxygen fugacity in high-pressure experiments

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Abstract. We present new models for the activity of iron ($\gamma_{\text{Fe}}$) in solid face-centered cubic (fcc) and liquid FePt alloy at high temperature and pressure to facilitate their use as sliding buffer redox sensors under extreme conditions. Numerous experimental studies of $\gamma_{\text{Fe}}$ in FePt alloy at 100 kPa have produced a wide spread of values. By favoring high-temperature studies that are more likely to have produced equilibrium measurement and excluding experiments for compositions and temperatures that probably encountered ordered or unmixed low-temperature phases, we regress an asymmetric Margules activity–composition model with parameters $W_{\text{fcc \ FePt}} = -121.5 \pm 2.1 \text{ kJ mol}^{-1}$ and $W_{\text{fcc \ PtFe}} = -93.3 \pm 4.3 \text{ kJ mol}^{-1}$. These values are close to the widely used model of Kessel et al. (2001), but for Pt-rich compositions they predict larger Fe activities and correspondingly more reduced oxygen fugacities. Activity–composition relations in liquid FePt are calibrated from direct measurements of activities and, most sensitively, from the trace of the Fe–Pt liquidus. Together, these yield asymmetric Margules parameters of $W_{\text{liq \ FePt}} = -124.5 \text{ kJ mol}^{-1}$ and $W_{\text{liq \ PtFe}} = -94.0 \text{ kJ mol}^{-1}$. The effects of pressure on both fcc and liquid FePt alloy are considered from excess-volume relations. Both solid and liquid alloy display significant positive excess volumes of mixing. Extraction of the excess volume of mixing for fcc FePt alloy requires filtering data for ordered low-temperature phases and corrections for the effects of magnetostriction on Fe-rich compositions which exhibit “Invar” behavior. Applied at high temperatures and pressures, both solid and liquid FePt alloys have strongly negative deviations from ideality at low pressure, which become closer to ideal at high pressure. These models provide a provisional basis for the calculation of $a_{\text{Fe}}$ in high-temperature, high-pressure experiments that, when combined with estimates of $a_{\text{FeO}}$, allow characterization of $f_{\text{O2}}$ under conditions relevant to magma oceans, core formation, and differentiation processes in the lower mantle of Earth or on other terrestrial planets. Improvements in these models require new constraints on the equation of state of FePt fcc alloy and documentation of the high-pressure melting relations in the system Fe–Pt.


2 Fe activity in FePt alloy as an $f_{O_2}$ sensor

Characterization of the oxygen fugacity prevailing in high-temperature, high-pressure apparatuses can be of great importance to experimental studies of phase equilibria, element partitioning, volatile solubilities, and transport properties (Cline et al., 2018; Otsuka et al., 2013; Yoshino et al., 2020). However, direct control of $f_{O_2}$ in experimental assemblages, for example through the coexistence of well-defined $f_{O_2}$ buffers, is not always feasible. An alternative strategy is to design experiments so that the $f_{O_2}$ can be determined afterwards, based on the compositions of “sliding buffers” (Taylor et al., 1992) incorporating solid solutions with components that participate in buffer reactions. These sliding buffers include alloys between a base metal (Fe, Ni, Co), which participates in the buffer reaction, and one or more noble metals (Pt, Pd, Ir, Au) (Balta et al., 2011; Grove, 1981; Taylor et al., 1992; Woodland and O’Neill, 1997). One of the most common of these is FePt alloy, which through coexistence with assemblages with known activity of FeO, $a_{FeO}$, monitors $f_{O_2}$ by the reaction

$$Fe + 1/2 O_2 \leftrightarrow FeO_{oxide, silicate},$$

(1)

for which the $f_{O_2}$ is given by

$$\log f_{O_2} = 2 \left( \frac{a_{FeO}}{a_{Fe}} - \frac{\Delta G^0}{RT \ln 10} \right)$$

(2)

(Grove, 1981; Medard et al., 2008; Gudmundsson and Holloway, 1993; Kessel et al., 2001) and where $\Delta G^0$ is the free energy difference between the pure reactants at the temperature and pressure of interest.

The activity of FeO in Eq. (2) may be characterized from activity coefficients of FeO in silicate melts (Kessel et al., 2001; Doyle, 1988; O’Neill and Eggins, 2002; Holzheid and Grove, 2005; Hirschmann, 2022) or by coexistence of FeO-bearing minerals such as olivine and orthopyroxene (Jamieson et al., 1992; Stanley et al., 2014). Medard et al. (2008) presented an empirical calibration, applicable to modest pressure conditions, in which they combined the non-ideal effects of FeO and the value of $\Delta G^0$.

The activity of Fe in FePt alloy, $a_{Fe}$, is given by

$$a_{Fe} = \gamma_{Fe} X_{Fe},$$

(3)

where $X_{Fe}$ and $\gamma_{Fe}$ are the mole fraction and the activity coefficient of Fe. As the thermodynamic mixing properties of FePt alloy are highly non-ideal, $\gamma_{Fe}$ can be $\ll 1$, particularly for Pt-rich alloy compositions (Larson and Chipman, 1954; Gudmundsson and Holloway, 1993; Kessel et al., 2001).

The activity coefficient, $\gamma_{Fe}$, is given by

$$RT \ln \gamma_{Fe} = G^{XS} + (1 - X_{Fe}) \left( \frac{\partial G^{XS}}{\partial X_{Fe}} \right).$$

(4)
where $G^{XS}$ is the excess free energy of the solution, describing mixing effects in addition to ideal contributions from the configurational entropy:

$$G = X_FeG^{0}_{Fe} + X_{Pt}G^{0}_{Pt} + RT(X_{Fe}lnX_{Fe} + X_{Pt}lnX_{Pt}) + G^{XS}.$$  \tag{5}

Previous treatments of solid and liquid FePt alloys have found $G^{XS}$ to be well-described by a power expansion to third order, in either Redlich–Kister (Fredriksson and Sundman, 2001; Heald, 1967; Gudmundsson and Holloway, 1993) or Margules (Kessel et al., 2001) formulations. Here we adopt the Margules approach:

$$G^{XS} = (W_{FePt}X_{Pt} + W_{PtFe}X_{Fe})X_{Pt}X_{Fe},$$  \tag{6}

$$RT ln\gamma_{Fe} = (W_{FePt} + 2(W_{PtFe} - W_{FePt})X_{Fe})X_{Pt}.$$  \tag{7}

Calculations of $\gamma_{Fe}$ at high pressure may require incorporation of the effects of pressure on non-ideal mixing. The pressure effect is given by the excess volume of mixing, $V^{XS}$, as

$$\left(\frac{\partial G^{XS}}{\partial P}\right)_T = V^{XS},$$  \tag{8}

and so

$$G^{XS} = G^{XS}_{P_0} + \int_{P_0}^{P} V^{XS}_dP.$$  \tag{9}

Values of $V^{XS}$ are non-zero if the volume of the FePt alloy, $V_{FePt}$, is not a linear combination of the volumes of the pure endmembers, $V_{Fe}$ and $V_{Pt}$, i.e., if

$$V^{XS} = V_{FePt} - X_{Fe}V_{Fe} - X_{Pt}V_{Pt} \neq 0.$$  \tag{10}

Similarly to $G^{XS}$, $V^{XS}$ can be modeled with a Margules-like function:

$$V^{XS} = \left(W^V_{FePt} + W^V_{PtFe}\right)X_{Fe}X_{Pt}.$$  \tag{11}

If $V^{XS}$ is not a function of pressure, then

$$G^{XS} = G^{XS}_{P_0} + V^{XS}(P - P_0).$$  \tag{12}

We will examine this assumption in the Discussion. Combining Eqs. (6), (11), and (12), the coefficients for the calculation of activity coefficients at the pressure of interest then become

$$W_{AB,P} = W_{AB,P_0} + W^V_{AB}(P - P_0).$$  \tag{13}

As described below, numerous studies have characterized $\gamma_{Fe}$ in solid FePt alloy at 100 kPa, and these have been used to characterize $f_{O_2}$ at modest pressure in piston cylinder or multi- anvil devices. With a few exceptions (Rubie et al., 1993; Stagno et al., 2015; Davis and Cottrell, 2021), such pressure corrections are seldom applied. Neglecting pressure effects for experiments at modest pressure, for example those in piston cylinder devices at 1–3 GPa, may be justified. Gudmundsson and Holloway (1993) determined activities of Fe in FePt alloy at 2 GPa and found general agreement with results from their 100 kPa experiments. On the other hand, the actual differences from 100 kPa values at this modest pressure may have been too small to overcome potential inaccuracies in $f_{O_2}$ arising from comparison between buffering in gas mixing and solid media experiments. Similarly, based on excess-volume estimates, Kessel et al. (2001) recommended that the effects of pressure may not be consequential below 4 GPa. However, the magnitude of effects at moderate pressure should be better quantified, and for application to higher-pressure conditions, non-ideal volume effects on activities of Fe in FePt alloys are likely to be important and need evaluation.

In experiments at high temperature, FePt alloy may be molten, requiring adjustment for differences in properties between solid and liquid alloy. The minimum melting temperature of FePt alloy is approximated by the fusion temperature of pure Fe, and at high temperature, the bound is fusion of pure Pt (Fig. 1). Experiments at more reduced conditions produce more Fe-rich alloys, and therefore the transition to molten alloys occurs at higher temperature, closer to the fusion temperature of pure Pt, for more oxidized conditions.

Constraints on the thermodynamic properties of molten FePt alloys include Knudsen cell measurements of Fe activities (Alcock and Kubik, 1968) and those that can be inferred from the properties of solid FePt alloy by matching Fe–Pt melting relations (Buckley and Hume-Rothery, 1959; Fredriksson, 2004; Isaac and Tammann, 1907). We are aware of two previous thermodynamic models for the thermodynamic mixing properties of molten FePt alloy, those of Fredriksson and Sundman (2001) and Odusote (2008), but each has some unsatisfactory features. The Odusote (2008) model is, unfortunately, calibrated only from data on FePt solid at 1123 K and therefore is not necessarily applicable to liquid solutions. Fredriksson and Sundman (2001) calibrated a Redlich–Kister model based on both the Knudsen cell and melting-loop data. However, their model, calibrated from data over a relatively modest temperature interval (1775–1950 K), adopts a strong temperature dependence on the mixing properties. As a consequence, extrapolation to high temperature predicts increasing values for the activity coefficient of Fe that are not based on experimental constraints and are unexpected based on usual thermodynamic theory. For example, for alloy with $X_{Fe} = 0.1$, Fredriksson and Sundman (2001) predict $\gamma_{Fe}$ values at 2000, 3000, and 4000 K of 0.004, 0.28, and 2.23, respectively.
3 Constraints on FePt alloy thermodynamics

3.1 Activity–composition relations in FePt alloy at 100 kPa

Activities of Fe in solid FePt alloy have been investigated at 100 kPa by EMF, Knudsen cell mass spectrometry, and equilibration with an Fe oxide at known oxygen fugacity (Table 1). We also consider experiments at 2 GPa in which alloy was equilibrated with pairs of coexisting Fe oxides, which thereby fixed the activity of Fe (Gudmundsson and Holloway, 1993). For these experiments, we adjusted observed values of $RT \ln \gamma$ down to 100 kPa equivalents using the volume interaction parameters described in the next section.

Experimentally determined activity coefficients of Fe show a significant spread of values (Fig. 2). The studies fall into two groups, as indicated in Table 1 and Fig. 2. Group 1 studies were conducted mostly at high temperature (1200–1550°C), except that of Alcock and Kubik (1969) (850–1000°C); yield activity coefficients that are comparatively small at a given FePt composition; and are broadly consistent with one another. Group 2 studies are mostly from lower temperature, 700–1298°C, except data from Vrestal (1973) (1427°C), and scatter to larger values of $\gamma_{Fe}$ at a given composition. The distinctions between these two groups are not obviously traceable to differences in the experimental technique. Lower-temperature experiments in Group 2 with intermediate compositions ($0.2 \leq X_{Fe} \leq 0.6$) may have been conducted within the region of stability of ordered FePt phases, Pt$_7$Fe (isoferr platinum) or FePt (tetraferro platinum) (Cabri et al., 2022), yielding either different chemical potentials of Fe or unmixing of alloy to produce disordered face-centered cubic (fcc) alloy with a composition distinct from the bulk material (e.g., Fredriksson and Sundman, 2001). Alternatively, the lower-temperature phases may have failed to reach equilibrium, which can be slow even at relatively high temperature (Taylor and Muan, 1962). We therefore focus only on Group 1 experiments.

We first fit the data from Group 1 to an asymmetric regular solution model, (Eq. 7), with regressed parameters $W^{\text{FePt}}_{\text{fcc}} = -121.9 \pm 2.1$ kJ mol$^{-1}$ and $W^{\text{PtFe}}_{\text{fcc}} = -91.0 \pm 3.8$ kJ mol$^{-1}$ (Fig. 2). However, some of the compositions in these experiments may also have undergone unmixing or formation of ordered phases, as the stability of isoferr platinum and tetraferro platinum extends to 1350 and 1275°C, respectively (Cabri et al., 2022). Of the 117 observations in the group, 20 plot within the temperature–composition fields of unmixed or ordered phases according to the phase diagram of Cabri et al. (2022). Therefore, we regressed independently the 97 observations that plot in the fcc field, yielding interaction parameters ($W^{\text{FePt}}_{\text{fcc}} = -121.5 \pm 2.1$ kJ mol$^{-1}$ and $W^{\text{PtFe}}_{\text{fcc}} = -93.3 \pm 4.3$ kJ mol$^{-1}$). The two sets of parameters are similar, indicating that the effect of phase diagram complexities on measured activities at high temperature is minimal. We adopt the set of parameters from the observations outside of miscibility gaps as the best approximation of $\gamma_{Fe}$ from Group 1 data (Table 2).

The regressed parameters are broadly similar to those from the widely used thermodynamic model of Kessel et al. (2001) ($W^{\text{FePt}}_{\text{fcc}} = -138 \pm 3.3$ kJ mol$^{-1}$; $W^{\text{PtFe}}_{\text{fcc}} = -90.8 \pm 24.0$ kJ mol$^{-1}$) (Table 2), and the two different curves predict similar $\gamma_{Fe}$ values for much of the compositional range, but they diverge at Fe mole fractions below 0.2, with the model of Kessel et al. (2001) predicting larger deviations from ideality (Fig. 2). These lower values of $\gamma_{Fe}$ are near the lower bound of a spread of experimental values in the Group 1 experiments at low $X_{Fe}$ (Fig. 2). The reasons for these disagreements are not clear, as both high and low values within this population include modern studies that employed similar experimental and analytical techniques. Consequently, in subsequent calculations here we employ both the new fit and the model of Kessel et al. (2001), and in the Discussion we consider further the quantitative differences between the two.

Figure 2. Experimental determinations of the non-ideality of Fe, expressed as $RT \ln \gamma_{Fe}$, in fcc FePt alloy. For sources of data and a key to the references, see Table 1. All data are from 100 kPa except for the seven experiments at 2 GPa from Gudmundsson and Holloway (1993) that are marked with “+” and which have been adjusted for pressure as described in the text. The data are divided into two groups, Group 1 studies, shown in filled symbols, were used to regress the thermodynamic model for FePt mixing. Group 2 studies, shown in unfilled symbols, were not used in calibration. Also data from Group 1 which plot inside the temperature–composition space of ordered FePt phases or in two-phase fields according to the phase diagram of Cabri et al. (2022) are not used in the final regression of interaction parameters and are plotted with smaller symbols (see text for explanation). The best fit to the remaining Group 1 data, regressed using Eq. (7), is shown with the black curve. Also shown is the fit given by Kessel et al. (2001) (dashed green curve).
Table 1. Summary of experimental determinations of Fe activities in FePt alloy compiled from the literature.

<table>
<thead>
<tr>
<th>Source</th>
<th>Symbol</th>
<th>Method</th>
<th>$T$ (°C)</th>
<th>$n_T(n_R)^*$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Larson and Chipman (1954)</td>
<td>LC54</td>
<td>Oxide–gas equilibration</td>
<td>1550</td>
<td>16(16)</td>
<td>100 kPa $\gamma_Fe$ as corrected by Kessel et al. (2001)</td>
</tr>
<tr>
<td>Taylor and Muan (1962)</td>
<td>TM62</td>
<td>Oxide–gas equilibration</td>
<td>1300</td>
<td>13(12)</td>
<td>Only the reduced half brackets are used; $\gamma_Fe$ as corrected by Kessel et al. (2001)</td>
</tr>
<tr>
<td>Gudmundsson and Holloway (1993)</td>
<td>GH93</td>
<td>Oxide–gas equilibration</td>
<td>1300–1400</td>
<td>29(27)</td>
<td>Includes seven experiments at 2 GPa; 100 kPa $\gamma_Fe$ as corrected by Kessel et al. (2001)</td>
</tr>
<tr>
<td>Petric and Jacob (1982), Petric et al. (1981)</td>
<td>PJ8182</td>
<td>Oxide–gas equilibration</td>
<td>1300–1400</td>
<td>8(6)</td>
<td></td>
</tr>
<tr>
<td>Kessel et al. (2001)</td>
<td>K01</td>
<td>Oxide–gas equilibration</td>
<td>1200–1400</td>
<td>23(19)</td>
<td></td>
</tr>
<tr>
<td>Henao and Itagaki (2007)</td>
<td>HI07</td>
<td>Oxide–gas equilibration</td>
<td>1300–1400</td>
<td>7(6)</td>
<td></td>
</tr>
<tr>
<td>Nikolic et al. (2008)</td>
<td>N08</td>
<td>Oxide–gas equilibration</td>
<td>1300</td>
<td>2(2)</td>
<td></td>
</tr>
<tr>
<td>Katahira and Hayashi (2016)</td>
<td>KH16</td>
<td>Oxide–gas equilibration</td>
<td>1300</td>
<td>5(5)</td>
<td></td>
</tr>
<tr>
<td>Group 2: not used for regression</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sundaresen et al. (1963)</td>
<td>S63</td>
<td>EMF</td>
<td>700–850</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Heald (1967)</td>
<td>H67</td>
<td>Oxide–gas equilibration</td>
<td>1141–1298</td>
<td>15</td>
<td>$\gamma_Fe$ as corrected by Kessel et al. (2001)</td>
</tr>
<tr>
<td>Vrestal (1973)</td>
<td>V73</td>
<td>Knudsen cell</td>
<td>1427</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Fredriksson and Seetharaman (2001)</td>
<td>FS01</td>
<td>EMF</td>
<td>850–1000</td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

* $n_T$ denotes the total number of measurements. For Group 1, $n_R$ denotes the number of measurements likely to be homogeneous fcc FePt and used for calibration.

Table 2. Interaction parameters for the thermodynamic models for fcc and liquid FePt alloy. The activity coefficient is given by $RT \ln \gamma_Fe = (W_{FePt} + 2(W_{PtFe} - W_{FePt})X_{Fe})X_{Pt}^2$ (Eq. 7). Pressure dependencies of interaction parameters are given by $W_{AB},P = W_{AB},P_0 + W_{V,AB}(P - P_0)$ (Eq. 13), where $P_0 = 100$ kPa.

<table>
<thead>
<tr>
<th></th>
<th>fcc FePt</th>
<th>Liquid FePt consistent with fcc properties from the following</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Kessel et al. (2001)</td>
<td>This study</td>
</tr>
<tr>
<td>$W_{FePt}$ (kJ mol$^{-1}$)</td>
<td>$-121.5 \pm 2.1$</td>
<td>$-138 \pm 3.3$</td>
</tr>
<tr>
<td>$W_{PtFe}$ (kJ mol$^{-1}$)</td>
<td>$-93.3 \pm 4.3$</td>
<td>$-90.8 \pm 24.0$</td>
</tr>
<tr>
<td>$W_{FePt},P_0$ (kJ mol$^{-1}$ GPa$^{-1}$)</td>
<td>$1.07 \pm 0.20$</td>
<td>1.75</td>
</tr>
<tr>
<td>$W_{PtFe},P_0$ (kJ mol$^{-1}$ GPa$^{-1}$)</td>
<td>$1.66 \pm 0.22$</td>
<td>1.75</td>
</tr>
</tbody>
</table>
3.2 Properties of liquid FePt alloy

Knudsen cell determinations of Fe activity in molten FePt alloy at 1819–1898 K from Alcock and Kubik (1968) indicate significant negative deviations from ideality which resemble those found for fcc alloy (Fig. 3). Unfortunately, the measurements include only compositions with $X_{Fe} \geq 0.4$, and therefore they do not constrain well the properties of Pt-rich alloys. However, a more complete picture of the mixing properties of molten FePt alloy can be gleaned from the topology of FePt melting relations.

Activity–composition relations for liquid FePt alloy can be described with the same asymmetric regular solution formalism as applied to fcc alloy (Eq. 7). A least-squares fit to the Knudsen cell data gives values of $W_{FePt}^{liq}$ and $W_{PtFe}^{liq}$ of $-200 \pm 140$ and $-90 \pm 40$ kJ mol$^{-1}$, respectively. As indicated by the magnitude of the uncertainties, these data do not yield statistically well-defined parameters and taken in isolation would be better described by a simpler one-parameter mixing model. However, when constraints from FePt solid–melt equilibrium are considered via the phase diagram, it is apparent that a two-parameter fit is needed.

The principal observations of the melting behavior of FePt alloy across its compositional range remain the pioneering experiments of Isaac and Tamman (1907), who defined distinct liquidus and solidus curves separated by up to 100 $^\circ$C (Fig. 4). Subsequent studies include melting experiments by Buckley and Hume-Rothery (1959), which are limited to compositions $0.925 \leq X_{Fe} \leq 1$, in the same region where both fcc and body-centered cubic (bcc) alloy are liquidus phases, and differential thermal analysis (DTA) for three compositions by Fredriksson (2004). The latter results are in excellent agreement with the liquidus defined by the original Isaac and Tamman (1907) experiments but provide no confirmation of their solidus. Unfortunately, Isaac and Tamman (1907) provided little detail about their solidus location and reveal to have relied principally on metallographic textures of quenched experimental products.

For analysis of the binary FePt melting loop, we consider the thermodynamics of solid (fcc) and molten Fe from the SGTE database of Dinsdale (1991). Unfortunately, the SGTE database has a $G$ function for fcc Pt that possesses a pronounced discontinuity near the fusion temperature, making calculations near the melting point unreliable. Instead,
we employ the properties of fcc and molten Pt from Arblaster (2005). Our analysis neglects the stabilization of the bcc phase, as this is stable only for very Fe-rich compositions and for a narrow span of pressures and temperatures (Buckley and Hume-Rothery, 1959; Komabayashi and Fei, 2010).

Owing to the small values of the enthalpy of fusion for Fe and Pt, the width of the calculated two-phase melting loop is expected to be extremely narrow. For example, Alcock and Kubik (1968) calculated that the region of solid and liquid coexistence should span less than 10°C. Fredriksson and Sundman (2001) also predicted a narrow melting loop < 5°C wide except for very Pt-rich compositions (X_{Fe} < 0.1), where their predicted melting loop becomes steep (Fig. 4). Given that the enthalpies of fusion of pure Fe and Pt are well-constrained, no combination of liquid activity coefficients could produce a topology with a substantially larger melting interval (Pelton, 2001). A narrow melting loop is consistent with the experimental study on Fe-rich compositions by Buckley and Hume-Rothery (1959) for Fe-rich compositions but inconsistent with the wider two-phase region inferred by Isaac and Tammann (1907). Because the DTA observations of Fredriksson (2004) affirm the liquidus trend of Isaac and Tammann (1907) and because the latter’s solids detection method is not known, we focused our fitting procedure on this feature and have not attempted to reproduce the solidus reported by the latter.

For an assumed set of mixing parameters for the solid fcc phase, together with endmember properties of Fe and Pt solid and liquid, the position and shape of the calculated liquidus are highly sensitive to the liquid mixing properties, and so fitting the liquidus allows refinement of the liquid parameters with small uncertainties. Using the mixing properties of fcc alloy regressed in this work, W_{FePt}^{liq} = -121.5 \text{kJ mol}^{-1} and W_{FeFe}^{liq} = -93.3, liquid parameters are W_{PtFe}^{liq} = -122.2 \text{kJ mol}^{-1} and W_{PfFe}^{liq} = -94.5 \text{kJ mol}^{-1} (Table 2). The solidus calculated with these same parameters, also shown in Fig. 4, tracks the liquidus curve quite closely and is displaced downward by ~ 5°C.

Figure 4 also shows the ±2 kJ mol\(^{-1}\) uncertainty envelopes about the fitted liquidus curve. As can be seen, the calculated liquidus at the extrema of these envelopes are displaced significantly from the experimentally determined liquidus locations such that varying one of the mixing parameters by 2 kJ corresponds to a displacement of the liquidus of approximately 50°C across much of the composition range. Therefore, though more plentiful modern determinations of the Fe–Pt melting loop would be welcome, they would not change the inferred mixing properties of FePt liquid by large amounts unless the revised melting temperatures were found to be quite different from those illustrated in Fig. 4. However, we note that these liquid parameter uncertainties cannot be smaller than the uncertainties in fcc interaction parameters, as variation in the latter maps nearly linearly to that of the former. Therefore, if the fcc parameters regressed in this work are considered to be the most accurate, the uncertainties in FePt liquid interaction parameters are, conservatively, ±4 kJ mol\(^{-1}\).

An alternative fit to the liquid interaction parameters can also be derived by adopting the fcc solid mixing parameters of Kessel et al. (2001). These reproduce the experimental melting relations with similar fidelity to the fit for the newly regressed parameters (inset, Fig. 4) but with liquid interaction parameters of W_{FePt}^{liq} = -140.8 \text{kJ mol}^{-1} and W_{PtFe}^{liq} = -93.2 \text{kJ mol}^{-1} (Table 2).

Both liquid parameter fits to the phase equilibria data (Fig. 4) predict activity coefficients in liquid FePt alloy that are reasonable matches to those determined from the Knudsen cell measurements (Fig. 3). In detail, both predict activity coefficients that are a little lower than most of the Fe-rich molten alloy Knudsen cell data, but the mismatches are close to analytical uncertainties. We therefore adopt the liquid alloy parameters derived from the position of the melting loop (Fig. 4) (Table 2), as the latter have great sensitivity to the experimental data.

### 3.3 The effect of pressure – excess volumes of mixing

Both synthetic and natural FePt alloys exhibit significant positive excess volumes (Fig. 5), though the latter offer less accurate measures owing to variable substitutions of additional base and platinum-group metals. Therefore we consider only synthetic alloys for parameterizing excess volumes of mixing. But first it is necessary to correct Fe-rich compositions for the effects of magnetostriction on ferromagnetic “Invar”-type alloys.

Ferromagnetic FePt alloys display the Invar effect, in which magnetostriction produces anomalous volumes relative to the paramagnetic disordered state (Wasserman, 1991). At 100 kPa, FePt alloys have Curie temperatures greater than room temperature for compositions approximately between Fe_{75}Pt_{25} and Fe_{30}Pt_{70} (Vlaic and Burzo, 2010; Ponomaryova et al., 2014), although above ~ 4 GPa they become paramagnetic at room temperature across their compositional range (Odin et al., 1999; Matsushita et al., 2004; Oomi and Mōri, 1981a). Density functional theory (DFT) calculations demonstrate that the anomalous volumes caused by the Invar effect are maximal near the peak of magnetization, which occurs at Fe_{75}Pt_{25} (Hayn and Drchal, 1998), and diminish significantly for more Fe- or Pt-rich solutions, such that they are negligible for compositions that are Pt-richer than Fe_{50}Pt_{50} (Khmelevskiy et al., 2003) and more Fe-rich than Fe_{75}Pt_{25} (Hayn and Drchal, 1998).

Figure 6 illustrates the effects of magnetostriction on FePt alloy volumes from both experiments (Franse and Gersdorf, 1986; Oomi and Mōri, 1981a; Odin et al., 1999) and molecular dynamics calculations (Khmelevskiy et al., 2005, 2003; Vlaic and Burzo, 2010). As noted by Khmelevskiy et al. (2005), theoretical calculations overpredict experimentally observed magnetostriction effects. Therefore, we correct experimen-
Excess volumes of mixing, \( V^{X} \), of synthetic and natural fcc structure FePt alloys at 298 K and of molten FePt alloy at 2000 K, both at 100 kPa. Synthetic fcc alloy data from Gudmundsson and Holloway (1993) (GH93), Gang et al. (2005) (G05), Cabri and Feather (1975) (CF75), Matsushita et al. (2004) (M04); Odin et al. (1999) (O99), Oomi and Mörí (1981a) (OM81), and Sedov (1987) (S87). Natural alloy data from Cabri and Feather (1975) and Malitch and Thalhammer (2002) (MT02). Vertical dashed lines join observed volumes of (open symbols) ferromagnetic fcc alloys with (solid symbols) volumes of paramagnetic phases of the same composition from the same study (Oomi and Mörí, 1981a), or extrapolated from high-pressure paramagnetic data (Matsushita et al., 2004; Odin et al., 1999), or volumes corrected for the effects of magnetostriction using Eq. (14) (Sedov, 1987; Gang et al., 2005). The solid curve gives the \( V^{X} \) function (Eq. 11), fit only to synthetic data for paramagnetic alloys and corrected ferromagnetic alloys (all shown as solid symbols). Natural crystals and uncorrected ferromagnetic crystals (all open symbols) were not used for the fit. Also shown are volumes of liquid FePt alloy at 2000 K (Watanabe et al., 2020) and the fit to those data (dashed curve) (Eq. 11). Values of \( V^{X} \) are calculated according to Eq. (10), where volumes of pure Fe and Pt were taken from the same study in which the FePt alloy volume was reported or, if not reported, was 6.835 cm\(^3\) mol\(^{-1}\) for Fe (Komabayashi and Fei, 2010) and 9.091 cm\(^3\) mol\(^{-1}\) for Pt (Arblester, 1997) at 100 kPa. We do not consider data from ordered low-temperature alloys such as isoferrplatinum and tetraferroplatinum, as their volumes are affected by the phase change and the thermodynamic mixing model of interest applies only to the fcc high-temperature phase. Considering only synthetic fcc phases, corrected where necessary for the effects of magnetostriction, we regress an excess-volume mixing relation based on Eq. (11), leading to values of \( W_{FePt}^{V^{X}} \) and \( W_{PtFe}^{V^{X}} \) of 1.07 \( \pm \) 0.20 kJ mol GPa\(^{-1}\) and 1.66 \( \pm \) 0.22 kJ mol GPa\(^{-1}\) (1 kJ GPa mol\(^{-1}\) = 1 cm\(^3\) mol\(^{-1}\)) (Table 2).

Figure 5. Excess volumes of mixing, \( V^{X} \), of synthetic and natural fcc structure FePt alloys at 298 K and of molten FePt alloy at 2000 K, both at 100 kPa. Synthetic fcc alloy data from Gudmundsson and Holloway (1993) (GH93), Gang et al. (2005) (G05), Cabri and Feather (1975) (CF75), Matsushita et al. (2004) (M04); Odin et al. (1999) (O99), Oomi and Mörí (1981a) (OM81), and Sedov (1987) (S87). Natural alloy data from Cabri and Feather (1975) and Malitch and Thalhammer (2002) (MT02). Vertical dashed lines join observed volumes of (open symbols) ferromagnetic fcc alloys with (solid symbols) volumes of paramagnetic phases of the same composition from the same study (Oomi and Mörí, 1981a), or extrapolated from high-pressure paramagnetic data (Matsushita et al., 2004; Odin et al., 1999), or volumes corrected for the effects of magnetostriction using Eq. (14) (Sedov, 1987; Gang et al., 2005). The solid curve gives the \( V^{X} \) function (Eq. 11), fit only to synthetic data for paramagnetic alloys and corrected ferromagnetic alloys (all shown as solid symbols). Natural crystals and uncorrected ferromagnetic crystals (all open symbols) were not used for the fit. Also shown are volumes of liquid FePt alloy at 2000 K (Watanabe et al., 2020) and the fit to those data (dashed curve) (Eq. 11). Values of \( V^{X} \) are calculated according to Eq. (10), where volumes of pure Fe and Pt were taken from the same study in which the FePt alloy volume was reported or, if not reported, was 6.835 cm\(^3\) mol\(^{-1}\) for Fe (Komabayashi and Fei, 2010) and 9.091 cm\(^3\) mol\(^{-1}\) for Pt (Arblester, 1997) at 100 kPa. We do not consider data from ordered low-temperature alloys such as isoferrplatinum and tetraferroplatinum, as their volumes are affected by the phase change and the thermodynamic mixing model of interest applies only to the fcc high-temperature phase. Considering only synthetic fcc phases, corrected where necessary for the effects of magnetostriction, we regress an excess-volume mixing relation based on Eq. (11), leading to values of \( W_{FePt}^{V^{X}} \) and \( W_{PtFe}^{V^{X}} \) of 1.07 \( \pm \) 0.20 kJ mol GPa\(^{-1}\) and 1.66 \( \pm \) 0.22 kJ mol GPa\(^{-1}\) (1 kJ GPa mol\(^{-1}\) = 1 cm\(^3\) mol\(^{-1}\)) (Table 2).

Figure 6. The magnetostriction effect of the ferromagnetic-to-paramagnetic transition on molar volume for ferromagnetic fcc FePt alloys between 0.5 \( \leq X_{Fe} \leq 0.75 \). Magnetostriction is negligible for compositions outside this compositional range (Hayn and Drchal, 1998; Khmelevskyi et al., 2003). Ab initio calculations, shown with dashed lines connecting individual compositions, are from Khmelevskyi et al. (2003) (K03), Khmelevskyi et al. (2005)(K05), and Vlaic and Burzo (2010) (VB10), and experimental determinations are from Odin et al. (1999) (O99), Nataf et al. (2006) (N06), Oomi and Mörí (1981a) (OM81), and Franse and Gersdorf (1986) (FG86). For this compositional interval, corrections for the effect of magnetostriction on excess volumes of mixing of ferromagnetic fcc FePt alloys are calculated with the line labeled “fm/pm” (Eq. 14).

Based on density measurements for \( X_{Fe} = 0.5 \), \( X_{Fe} = 0.75 \), and pure Fe and Pt liquids at 1753–2354 K (Watanabe et al., 2020), liquid FePt alloys also have positive excess volumes of mixing (Fig. 5) which exceed those found for fcc alloys. Owing to the small number of constraints, these are best parameterized by a single symmetric excess volume of mixing of \( W_{FePt}^{V^{liq}} = W_{PtFe}^{V^{liq}} = 1.75 \) kJ mol GPa\(^{-1}\) (Fig. 5) (Table 2).

4 Results

Activity coefficients of Fe, \( \gamma_{Fe} \), in fcc FePt alloy, calculated at 2000 K with the values of \( W_{FePt}^{V^{X}} \) and \( W_{PtFe}^{V^{X}} \) regressed in this work, are shown in Fig. 7a as a function of composition and pressure. Strongly negative deviations from ideality in Pt-rich compositions at low pressure, expressed as small values of \( \gamma_{Fe} \), become less pronounced with increasing pressure. The pressure dependence of \( \gamma_{Fe} \) produces a decrease in calculated oxygen fugacity, relative to the iron–wüstite or similar \( fO_{2} \) buffer, for FePt alloy of a given composition coexisting with an assemblage that imposes a particular chemical potential of FeO (Fig. 7b). The latter could be olivine coexisting with orthopyroxene (Jamieson et al., 1992) or a
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silicate melt for which the activity coefficient of FeO can be estimated (Kessel et al., 2001; Medard et al., 2008). As previously noted by Kessel et al. (2001), the pressure effect is relatively small at moderate pressures imposed by piston cylinder experiments. For example, the pressure correction to log $f_{O_2}$ at 3 GPa and 1400°C amounts to no more than 0.2 log units. But it becomes more pronounced at higher pressure, exceeding 2 log units for Pt-rich compositions above 40 GPa (Fig. 7b).

Because the thermodynamic mixing properties of liquid and solid FePt are quite similar, activity coefficients for liquid are nearly indistinguishable from those of the solid at a given composition and temperature, albeit relative to a liquid rather than solid standard state. Activity coefficients calculated at 3000 K for FePt liquid are shown in Fig. 7c. Comparison to Fig. 7a shows relatively large values $\gamma_{Fe}$ for liquid compared to solid at 0 GPa, owing to the nearly more ideal behavior at higher temperature. As pressure increases, increases in $\gamma_{Fe}$ for liquid are more pronounced than for solid (i.e., the isobars are spaced further apart in Fig. 7c compared to Fig. 7a), owing to larger excess volumes of mixing (Fig. 5). Consequently, FePt liquid approaches ideal mixing at approximately 60 GPa.

5 Discussion

5.1 Comparison to model of Kessel et al. (2001)

As previously mentioned, the new model for $\gamma_{Fe}$, regressed in this work from all of the “Group 1” studies, is quite similar to the Kessel et al. (2001) model, derived only from the experiments in that investigation, but the two diverge for Pt-rich compositions (Figs. 2, 7). At 1400°C, the Kessel et al. (2001) model gives values of $\gamma_{Fe}$ that are 0.17, 0.32, and 0.49 log units lower than the preferred model at $X_{Fe} =$ 0.2, 0.1, and 0.01, respectively. For the calculation of oxygen fugacities, all other parameters being equal, this translates to values of $f_{O_2}$ that are 0.34, 0.64, and 0.99 log units more reducing. These differences are large enough to be potentially testable in experiments for which either $a_{Fe}$ or log $f_{O_2}$ is measured by other means.

Klemettinen et al. (2021) measured $a_{Fe}$ in spinel-saturated slags over a range of oxygen fugacities using both FePt and FePd alloy as sensors. They calculated $a_{Fe}$ from FePt compositions using the model of Kessel et al. (2001) and from FePd sensors using the model of Ghosh et al. (1999). The two sensors show excellent agreement under reducing conditions, corresponding to Fe-rich alloys, but diverged under more oxidizing conditions and Pt-rich alloys (Fig. 8). Recalculating $a_{Fe}$ from the FePt alloys using the regressed model from this work improves agreement with the FePd sensor. At log $f_{O_2} =$ −6, corresponding to alloy with $X_{Fe} =$ 0.14, the Kessel et al. (2001) model gives an $a_{Fe}$ value 0.7 log units lower than the FePd sensor, whereas the new regressed model

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Figure 7. (a) Calculated activity coefficient of Fe, $\gamma_{Fe}$, in fcc FePt alloy as a function of composition and pressure at 2000 K. For calculations at low pressure with iron-rich compositions, the calculated fcc phase is metastable relative to liquid FePt. Alloys have strong negative deviations from ideality at low pressure, particularly at low bulk Fe content, but with increasing pressure, the excess volume of Fe–Pt mixing (Fig. 5) strongly moderates this effect. (b) The pressure effect on $\gamma_{Fe}$ for fcc FePt manifested in calculated log $f_{O_2}$. For a given assemblage with known chemical potential of FeO (i.e., wüstite, olivine + orthopyroxene, silicate melt) coexisting with fcc FePt alloy, this calculation shows how the resulting log $f_{O_2}$ is affected by the pressure effect on $\gamma_{Fe}$ in comparison to the results of the same calculation if the pressure effect is neglected. (c) Calculated activity coefficient of Fe in liquid FePt alloy as a function of composition and pressure at 3000 K from 0 to 60 GPa. For calculations at high pressure with Pt-rich compositions, the calculated liquid phase is metastable relative to fcc FePt. Also shown are liquid activities at 0 and 3000 GPa calculated with the alternative liquid model calibrated against the fcc model of Kessel et al. (2001) (K01) and with the thermodynamic models of Fredriksson and Sundman (2001) (FS01) and Odusote (2008) (O08).
gives an \(a_{Fe}\) value only 0.3 log units lower. Thus, the new model improves consistency with activities of Fe determined from FePd alloys.

Davis and Cottrell (2021) compared values of \(\log f_{O_2}\) calculated from FePt alloy, using Kessel et al. (2001), and the FeO component in quenched silicate melts in experiments at 1380–1400 °C and 1.5 GPa with those determined from the same experiments by both spinel–olivine–orthopyroxene oxybarometry (Mattioli and Wood, 1988) and silicate melt oxybarometry (Kress and Carmichael, 1991), with the latter based on measurements of \(Fe^{3+}/Fe^{2+}\) in the quenched glasses. They found close agreement between \(f_{O_2}\) determined from alloy–melt equilibria and from spinel oxybarometry, with the former averaging 0.17 log units more oxidized than the latter (\(n = 5\)), but alloy-melt fugacities were on average 0.65 log units more oxidized than those from melt oxybarometry (\(n = 12\)) (Fig. 9). Recalculating with the newly regressed alloy-melt model yields oxygen fugacities averaging 0.43 log units more reduced than the spinel oxybarometry and 0.05 more oxidized than the melt oxybarometer (Fig. 9). Thus, compared to the model of Kessel et al. (2001), the regressed model is less congruent with spinel oxybarometry but in better agreement with melt oxybarometry. As noted by Davis and Cottrell (2021), spinel oxybarometry may be more accurate at 1.5 GPa than the melt oxybarometer of Kress and Carmichael (1991). However, we note that for both alloy models, as \(X_{Fe}\) in the alloy becomes smaller (which is to say, as conditions become more oxidized), the oxygen fugacity calculated with the alloy-melt oxybarometer becomes more oxidized relative to those calculated from both spinel oxybarometry and melt oxybarometry (i.e., the trends for all four have negative slopes in Fig. 9). This indicates that there may be an unidentified systematic contribution to the mismatches.

Given these comparisons, it is not clear whether the newly regressed alloy model or that of Kessel et al. (2001) is most accurate. Additional studies allowing for further comparisons are needed.

5.2 Comparison to previous models for liquid FePt

Comparison of the newly derived model for liquid FePt alloy to those proposed by Fredriksson and Sundman (2001) and Odusote (2008) shows that these previous studies predict significantly larger activity coefficients at 3000 K and 0 GPa (Fig. 7). In the case of Fredriksson and Sundman (2001), this is owing to a strong temperature dependence on interaction parameters, as at more modest temperatures, this model predicts non-ideality similar to those from this work (Fig. 4). On the other hand, the Odusote (2008) model implies smaller deviations from ideality at all temperatures (Figs. 3 and 7).

Fredriksson and Sundman (2001) calculated melting relations for FePt alloy that are quite distinct from those modeled here. Although they also found that the melting interval is extremely narrow, their calculated liquidus is at consider-
ably lower temperature (Fig. 4). For Fe-rich compositions it is 25°C lower, and for Pt-rich compositions it is more than 100°C lower. Their melting interval is close to the solidus reported by Isaac and Tammann (1907), and therefore it does not reproduce the liquidus defined by the experiments of Isaac and Tammann (1907) or Fredriksson (2004).

5.3 Excess volume of fcc FePt at high pressure

Equation (13) is appropriate for the calculation of activities of Fe and Pt at high pressure if $V^{XS}$ can be assumed to be independent of pressure. Thermodynamic models of activity–composition relationships in solids and relatively incompressible fluids (e.g., molten alloys, oxide, or silicate liquids) typically make this assumption, whereas models for more compressible solutions, such as C–O–H–X mixed fluids, do not (e.g., Duan et al., 2008). Particularly for extrapolation to the high pressures that prevail in Earth’s deep mantle, there is no a priori justification for making the approximation in Eqs. (12) and (13), and so it is desirable to discern how excess volumes of mixing of FePt alloys are affected by pressure.

Because of the interest in volumetric and magnetic behavior of FePt Invar alloys near the composition Fe$_3$Pt, several studies have investigated the effect of pressures up to 26 GPa on volumes of fcc FePt alloys with $X_{Fe} = 0.7$ or 0.72 (Matsushita et al., 2004; Odin et al., 1999; Oomi and Mõrõ, 1981b). Ko et al. (2009) determined the equation of state for alloy with $X_{Fe} = 0.5$ up to 55 GPa, but they investigated the ordered tetragonal phase rather than fcc alloy. Observed high-pressure volumes of fcc FePt can be converted to values of $V^{XS}$ from Eq. (6), with high-pressure volumes of pure Fe and Pt from appropriate equations of state (Zha et al., 2008; Komabayashi and Fei, 2010). Interpretation is complicated by the influence of magnetostriction on ferromagnetic fcc alloys with $X_{Fe} = 0.7$ or 0.72, but above $\sim$ 4 GPa, these effects are absent as the alloys become paramagnetic at 300 K (Oomi and Mõrõ, 1981a). Therefore, the volumes of higher-pressure paramagnetic phases can be compared to 100 kPa volumes by correction of the latter for the effects of magnetostriction, as described by Eq. (14).

Unfortunately, these studies do not provide a coherent picture of the effects of pressure on $V^{XS}$ of FePt alloys. Whereas the data of Odin et al. (1999) indicate that $V^{XS}$ is nearly constant up to 10 GPa and then increases sharply up to 26 GPa, the highest pressure of that study, those of Oomi and Mõrõ (1981b) and Matsushita et al. (2004), up to 7 and 13 GPa, respectively, indicate that $V^{XS}$ decreases with pressure (Fig. 10). Values of $V^{XS}$ calculated from the data of Matsushita et al. (2004) have an apparent minimum between approximately 6–11 GPa and hint at an increasing trend in a single datum at 13 GPa. Thus, it seems that pressure variations in $V^{XS}$ are small or negative up to approximately 10 GPa and then increase significantly at greater pressures. If this is the case, then values of $\gamma_{Fe}$ calculated in this study (Fig. 7a) are underestimates at lower mantle pressures and calculated values of $f_{O_2}$ will be overestimates. However, the data in Fig. 10, with limited compositional range and significant interlaboratory discrepancies, are too fragmentary to formulate a model more complex than that given by Eqs. (12) and (13). Additional studies with a greater range of pressures and fcc alloy compositions are needed to better refine the effects of pressure on $a_{Fe}$ in FePt alloy.

5.4 Prospects for improved model for liquid FePt

Constraints on the thermodynamic mixing properties of FePt liquid alloy remain limited, regarding both mixing properties at 100 kPa (Fig. 3) and volumetric properties required for extrapolation to high pressure. Whilst further characterization of volumetric properties of liquid alloy, particularly at high pressure, is desirable, it is likely more tractable that improved resolution of the activity of Fe in molten FePt would be attained from accurate characterization of the melting relations in the Fe–Pt system, particularly at high pressure. As demonstrated by the thermodynamic calculations displayed in Fig. 4, the topology of the Fe–Pt liquidus is highly sensitive to Fe–Pt mixing properties of the solid and liquid. As the equations of state of pure Pt and Fe are well-studied (Dorogokupets et al., 2017; Jin et al., 2011; Komabayashi, 2014; Zha et al., 2008), high-pressure studies of the melting across the FePt phase loop would give strong constraints on activity–composition relations in FePt liquid, provided that they were combined with improved characterization of the equation of state of FePt solid alloy.
6 Conclusions

A reexamination of all the experimental data known to us for activities of Fe in fcc FePt alloy allows reevaluation of the mixing properties. Low-temperature studies produce larger and more dispersed values of $\gamma_{Fe}$, which we attribute to either the complexities introduced by the stabilization of ordered Fe–Pt intermetallic alloys or experimental durations insufficient to achieve equilibrium. Considering only the high-temperature data and filtering these for conditions potentially affected by intermetallic stabilization yield a new thermodynamic parameterization. Resulting activity coefficients are similar to those predicted by Kessel et al. (2001) but diverge to larger values for Pt-rich compositions. Experimental data available to evaluate which of these two models are more accurate, at present, equivocal conclusions.

Non-ideal mixing of liquid Fe–Pt alloy is tightly constrained by the position of the liquidus, provided that the properties of the coexisting fcc alloy are known. Activity coefficients of Fe in liquid alloy are very similar to those in fcc alloy for the same composition and temperature. Owing to the small enthalpies of fusion of Fe and Pt metal, the temperature interval for coexisting solid and liquid alloy is extremely narrow, amounting to $\sim 5^\circ C$.

Significant excess volumes of mixing for both fcc solid and liquid FePt alloy produce increased activity coefficients with increasing pressure, especially for Pt-rich compositions. Under lower-mantle conditions, this can enhance evaluated $\log f_{O_2}$ by several orders of magnitude. However, the pressure dependence of excess volumes is not well-constrained, and further investigation of the equation of state of FePt alloys is needed.

Code and data availability. The MATLAB code used to calculate Fig. 4 is provided in the Supplement. All data used have been published previously in the cited publications.

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/ejm-35-789-2023-supplement.

Author contributions. MMH and HZL mutually recognized the need for a model to calculate Fe activities in solid and liquid FePt at high pressure and examined previous work to evaluate its applicability. MMH compiled the data, did the thermodynamic modeling, prepared the figures, and wrote the original draft of the manuscript. MMH and HZL together weighed how to evaluate conflicting data and models and how best to approach an objective presentation. HZL edited and improved the original manuscript draft.

Competing interests. The contact author has declared that neither of the authors has any competing interests.

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