



The Gibbs energy formulation of α , γ , and liquid Fe_2SiO_4 using Grover, Getting, and Kennedy's empirical relation between volume and bulk modulus

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Abstract—The empirical linear relation between the volume and logarithm of bulk modulus of metals, discovered by Grover, Getting, and Kennedy is taken as the basis for our equation of state. Recently, we have shown that we can use this equation of state to make accurate predictions of thermochemical and thermophysical properties at high pressure and high temperatures for MgO and the polymorphs of Mg_2SiO_4 . Using the available experimental information, the equation of state is applied to the two polymorphs and the liquid form of Fe_2SiO_4 to develop a consistent dataset of their thermodynamic properties in the temperature range between 150 and 2500 K and pressure range between 1 bar–13 GPa. Using thermodynamic methods we are able to discriminate experimental data from different sources. The results presented here are compared with results obtained with modern databases. For $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$ solid solutions around a pyrolytic composition, we conclude that bulk sound velocity is not a strong discriminator in selecting Gibbs energy formulations for Fe_2SiO_4 using one database versus another. This is in contrast to what we found for Mg_2SiO_4 . Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Recently, we developed an equation of state based on the linear relationship between the volume and the logarithm of isothermal bulk modulus discovered by Grover et al. (1973). We applied this equation of state to the substances MgO and Mg_2SiO_4 and concluded that their thermodynamic properties at high pressure and temperature can be accurately described and predicted (Jacobs and Oonk, 2000a,b, Jacobs and Oonk, 2001a,b).

Currently, we are in the process of constructing a database based on this new equation of state. Emphasis is placed on a critical assessment of the complete collection of experimental data available to date, of all phases in the $\text{MgO-FeO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ system, which is of significance from a geodynamic perspective. Here we present our assessment of the α olivine, the γ spinel, and the liquid form of Fe_2SiO_4 .

Several earlier studies have been undertaken to develop an internally consistent database of the system MgO-FeO-SiO_2 , among which those of Fei et al. (1991), Saxena et al. (1993), and Fabrichnaya (1998). In our work, we incorporated new sources of experimental information on the volume of $\alpha\text{-Fe}_2\text{SiO}_4$. Using thermodynamic methods we were able to discriminate between experimental data on the adiabatic bulk modulus and the thermal expansivity of $\alpha\text{-Fe}_2\text{SiO}_4$ at 1 bar pressure.

We proceed by first presenting a short description of the new equation of state, its experimental background, and its function as starting point for calculating Gibbs energies. Next the significance of the results will be checked by comparing experimental data with calculated values for properties at high pressure. Finally we compare our results with those calculated

using various modern databases. Combining the results presented here with results for Mg_2SiO_4 leads to the conclusion that bulk sound velocity is not a strong discriminator in selecting Gibbs energy formulations for Fe_2SiO_4 using one database versus another.

2. THE EQUATION OF STATE AND GIBBS ENERGY FORMULATION

From shock-wave and static compression measurements on a variety of metals, Grover et al. (1973) found a “nearly precise linear relation” between the logarithm of bulk modulus and volume — up to volume changes of 40%. From this relationship we derived an equation of state, which we write as:

$$P = P^0 - K^0(T_0) \left\{ \exp \left(\frac{a(T_0 - T) - V^0(T_0)}{b} \right) \right\} \cdot \left[\ln \left(\frac{V}{V^0} \right) + \sum_{j=1}^{\infty} \left(\frac{b^{-j} (V^j - (V^0)^j)}{j * j!} \right) \right] \quad (1)$$

where V denotes molar volume, K the isothermal bulk modulus, T_0 a reference temperature, and the superscript “0” refers to standard pressure (1 bar). In Eqn. (1), a and b are material-dependent constants, and $V^0(T_0) = V(P^0, T_0)$ and $V^0 = V(P^0, T)$. We demonstrated (Jacobs and Oonk, 2000a,b, Jacobs and Oonk, 2001a,b) that this equation of state is capable of predicting accurately thermochemical and thermophysical properties of MgO and the polymorphs of Mg_2SiO_4 at high temperatures and pressures with at most three substance dependent parameters $K^0(T_0)$, a , and b . The parameter a is proportional to $(\partial K/\partial T)_V$ and is zero for MgO. For Mg_2SiO_4 however, it has been shown (Jacobs and Oonk, 2001b) that $(\partial K/\partial T)_V$ can reach values which are typically 20% of those for $(\partial K/\partial T)_P$. The

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parameter b is related to the pressure derivative of the isothermal bulk modulus, an important property in geophysics:

$$K' = \left(\frac{\partial K}{\partial P} \right)_T = -\frac{V}{b} \quad (2)$$

The volume V^0 is related to the thermal expansivity α^0 as:

$$V^0 = V^0(T_0) * \exp \left(\int_{T_0}^T \alpha^0 dT \right) \quad (3)$$

We used a polynomial function expression in temperature for α^0 , which is frequently used in geophysics, see e.g., Saxena et al. (1993).

The difference between our equation of state and those which are frequently used in geophysics and materials science, e.g., a Murnaghan or Birch-Murnaghan equation of state, is that, apart from the volume V^0 , the pressure-volume-temperature relation of a substance is described with only three substance dependent parameters, a , b , and $K^0(T_0)$. In a previous work on the polymorphs of Mg_2SiO_4 , Jacobs and Oonk (2001b), it has been shown that for the application of a Birch-Murnaghan equation of state

$$P = P^0 + \frac{3}{2} K^0 \left[\left(\frac{V}{V^0} \right)^{-7/3} - \left(\frac{V}{V^0} \right)^{-5/3} \right] \cdot \left\{ 1 - \frac{3}{4} (4 - K^{0'}) \left[\left(\frac{V}{V^0} \right)^{-2/3} - 1 \right] \right\} \quad (4)$$

four coefficients for the isothermal bulk modulus, K^0 , were needed to describe all experimental data within their error limits. In Eqn. (4), $K^{0'}$ denotes the pressure derivative, K' , at 1 bar pressure.

In the tables of the underlying paper we shall use the more familiar constants $V^0(T_0)$ and $K^{0'}(T_0)$. The constant b is calculated by substituting these values in Eqn. (2) giving $b = -V^0(T_0)/K^{0'}(T_0)$.

The molar Gibbs energy of a substance in a specific phase at arbitrary pressure and temperature conditions is written as:

$$G_m(T, P) = \Delta H_{f,m}^0 + \int_{T_0}^T C_{P,m}^0 dT - T \left\{ S_m^0 + \int_{T_0}^T \frac{C_{P,m}^0}{T} dT \right\} + \int_{P^0}^P V_m dP + G_{\text{disorder}} \quad (5)$$

where T denotes thermodynamic temperature, P pressure, $\Delta H_{f,m}^0$ the heat of formation, S_m^0 the absolute entropy. The last two properties are defined at reference temperature T_0 and reference pressure P^0 . $C_{P,m}^0$ is the heat capacity at 1 bar pressure and V_m denotes the molar volume. G_{disorder} denotes the contribution to the Gibbs energy resulting from cation disordering and is used here for $\gamma\text{-Fe}_2\text{SiO}_4$ only.

With the equation of state, Eqn. (1), and dropping the subscript ‘‘m,’’ the last integral term of Eqn. (5) becomes:

$$\int_{P^0}^P V dP = \int_{P^0, V^0}^{P, V} d(PV) - \int_{V^0}^V P dV = V(P - P^0) + K^0(T_0) \cdot \left\{ \exp \left(\frac{a(T_0 - T) - V^0(T_0)}{b} \right) \right\} * \left\{ V * \ln \left(\frac{V}{V^0} \right) - (V - V^0) \right\} + \sum_{j=1}^{\infty} \left[\frac{b^{-j}}{j * j!} \left(\frac{V^{j+1} - (V^0)^{j+1}}{j+1} - (V^0)^j (V - V^0) \right) \right] \quad (6)$$

where $V^0(T_0) = V(P^0, T_0)$ and $V^0 = V(P^0, T)$.

For $\gamma\text{-Fe}_2\text{SiO}_4$ with the spinel structure, we adopted Navrotsky's (1977) model, which takes cation disorder into account. This disorder is modeled by an ion exchange reaction indicating that Si^{4+} ions can move from tetrahedral to octahedral sites and Fe^{2+} ions from octahedral to tetrahedral sites. The interchange enthalpy for the reaction, ΔH_{int} , is the only adjustable parameter in the model. Navrotsky (1977) showed that it is reasonable to assume that ΔH_{int} is independent of temperature, pressure and the degree of disorder. Based on the work of Yagi et al. (1974), Navrotsky (1977) derived a value $+120.499 \text{ kJ}\cdot\text{mol}^{-1}$ for the interchange enthalpy. In a later work of Navrotsky et al. (1979) a value of $+119.662 \text{ kJ}\cdot\text{mol}^{-1}$ was determined based on the structure refinements of Marumo et al. (1977).

From the Gibbs energy defined by Eqn. (5), all thermodynamic properties used in this paper can be derived as a function of temperature and pressure.

3. OPTIMISATION STRATEGY

In Table 1, we give a summary of the data at 1 bar pressure used in our investigation. The enthalpy of formation and the absolute entropy at $P = 1$ bar and $T = 298.15$ K are available for $\alpha\text{-Fe}_2\text{SiO}_4$ in the compilation of Barin (1989). The heat capacity in this compilation is based on drop calorimetric measurements of Orr (1953) from room temperature up to the melting point. These data were fitted with a polynomial function. We used the same polynomial function expression as given by Richet and Fiquet (1991), to make high temperature extrapolations. The resulting expression for the Gibbs energy of $\alpha\text{-Fe}_2\text{SiO}_4$ at 1 bar pressure as a function of temperature is kept fixed in the thermodynamic analysis of the system. To relate the experimental data for the adiabatic bulk modulus, K_S , to the isothermal bulk modulus, K , needed for the application of Eqn. (1) and (6), we used the well known expressions $K_S = K(C_P/C_V)$ and $C_P - C_V = \alpha^2 K V T$, where C_V is the heat capacity at constant volume.

The difficulty in the analysis of the thermodynamic properties of $\alpha\text{-Fe}_2\text{SiO}_4$ lies in a considerable disagreement in the bulk modulus as well as thermal expansivity data. Thermodynamic analysis indicates that experimental V - P - T data, used in section 4, are well reproduced using the thermal expansivity data given by Suzuki et al. (1981) together with the adiabatic bulk modulus data of Sumino (1979). The results of our analysis coupling these two datasets will be referred to in the following as model A. Another assessment based on the ther-

Table 1. Summary of experimental data at 1 bar pressure used in this investigation. The abbreviation DSC stands for Differential Scanning Calorimetry and RPR for Rectangular Parallelepiped Resonance. ol denotes the olivine, and sp the spinel form of Fe_2SiO_4 .

Form	Property	Temperature range in K	Technique	Reference
ol	C_p	395–1481	Drop calorimetry	Orr (1953)
		136–383	Adiabatic calorimetry	Robie et al. (1982)
		350–700	DSC	Watanabe (1982)
	α	298–1490	Compilation	Barin (1989)
		298–1123	Dilatometry	Suzuki et al. (1981)
	K_S	293–1173	X-ray diffraction	Smyth (1975)
		293–673	RPR	Sumino (1979)
273–313		Pulse superposition ultrasonic method	Graham et al. (1988)	
sp	C_p	350–700	DSC	Watanabe (1982)
	α	273–2273	Grüneisen theory	Suzuki et al. (1979)
		281–669	X-ray diffraction	Mao et al. (1969)
	K_S	300	Pulse transmission	Mizutani et al. (1970)
		300	Pulse transmission	Akimoto (1972)
		300	Pulse superposition	Liebermann (1975)
		300	Pulse interferometry	Rigden/Jackson (1991)
liquid	C_p	1494–1724	Drop calorimetry	Orr (1953)
		1521–1705	Drop calorimetry	Stebbins/Carmichael (1984)
	V	1573–1873	Double bob Archimedean	Lange/Carmichael (1987)
	K	1573–1873	Double bob Archimedean	Lange/Carmichael (1987)
		1503 and 1653	ultrasonic	Rivers/Carmichael (1987)

mal expansivity data measured at 1 bar by Smyth (1975) together with the adiabatic bulk modulus data of Graham et al. (1988) leads to an even more accurate reproduction of all V - P - T data. The results of our analysis coupling these last two datasets will be designated model B. Other couples of adiabatic bulk modulus and thermal expansivity datasets lead to either a description of the V - P - T data outside the experimental error range or to negative thermal expansivity at pressures smaller than 30 GPa. As has been demonstrated by Jacobs and Oonk (2000b), such anomalous expansivity is associated with a minimum in the isothermal entropy-pressure curve and we consider it as a less favorable characteristic in the description of the system.

Model A and B lead to different behavior of thermal expansivity and bulk modulus as a function of pressure and temperature. Because these properties are important in geophysics, e.g., in determining sound velocities at the 400 km seismic discontinuity, we investigated the influence of the two models on the α - γ -liquid phase equilibria and the thermophysical properties of the liquid.

The heat of formation and absolute entropy of γ - Fe_2SiO_4 at 1 bar pressure and $T = 298.15$ K are unknown and the heat capacity (C_p) has been established over a limited temperature range. These properties were constrained by optimization of all available experimental data, such as volume, thermal expansivity, adiabatic bulk modulus, as a function of pressure and temperature, and the α - γ phase boundary data. Because of the phase boundary data, the two models A and B for α - Fe_2SiO_4 lead to different expressions for the Gibbs energy of γ - Fe_2SiO_4 . The interchange enthalpy, ΔH_{int} , needed to compute the contribution of cation disorder to the Gibbs energy of the spinel form was kept fixed to $120.499 \text{ kJ}\cdot\text{mol}^{-1}$. The resulting expressions for the Gibbs energies of the α and γ form were used to establish the Gibbs energy expression of liquid Fe_2SiO_4 . Just as for γ - Fe_2SiO_4 , the two models A and B for α - Fe_2SiO_4 lead to different expressions for the Gibbs energy of liquid Fe_2SiO_4 .

4. RESULTS OF THE THERMODYNAMIC PROPERTIES OF α - AND γ -POLYMORPHS

4.1. Thermodynamic properties at 1 bar pressure

We started the thermodynamic assessment with direct polynomial fits of the experimental heat capacity data of the α , γ and the liquid phase of Fe_2SiO_4 . To reach better agreement with the data above room temperature, we directed the optimization of the heat capacity of α - Fe_2SiO_4 towards the high temperature measurements of Orr (1953). As a consequence, the deviation of our result from the accurate heat capacity data or Robie (1982) becomes more than 1% at temperatures below 135 K. Therefore we restrict our thermodynamic description of the system to temperatures above 135 K. The results are given in Table 2. The quality of the fit of the experimental data is shown in Figure 1 and Table 3.

Details of the optimization for γ - Fe_2SiO_4 are given in section 5 and the result is given in Table 2. The calculated result is compared with experimental data in Figure 2.

4.2. Equation of state parameters for the α polymorph

The experimental data of Suzuki et al. (1981) for α - Fe_2SiO_4 were used to determine its thermal expansivity, the result of which is given in Table 2 labeled as model A and Figure 3. The expression for this property as derived from the volume-temperature (V - T) data at 1 bar pressure of Smyth (1975) is given in Table 2 labeled as model B and shown in Figure 3. The resulting thermal expansivity deviates substantially from the data of Suzuki et al. (1981) and to a lesser extent from the calculated result of Plymate and Stout (1990). In Figure 4 we compare the experimental volume data of Smyth (1975) with our calculated ones and the calculated result of Plymate and Stout (1990).

Figure 5 shows the disagreement between experimental adi-

Table 2. Thermodynamic properties at 1 bar of the three forms of Fe_2SiO_4 . The heat capacity C_p (expressed in $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) and thermal expansivity α (expressed in K^{-1}) are described with the polynomial function $F(T) = c_1 + c_2 * T + c_3 * T^{-1} + c_4 * T^{-2} + c_5 * \ln(T)$. ol denotes the olivine, and sp the spinel form of Fe_2SiO_4 .

Property	Form	c_1	c_2	c_3	c_4	c_5
C_p	ol	841.6142	8.4484×10^{-2}	-6.2430×10^4	3.01816×10^6	-98.1063
	sp ^{a)}	166.8428	3.7735×10^{-2}	-1.3911×10^4	-2.78277×10^5	
	sp ^{b)}	169.5058	3.2390×10^{-2}	-1.3911×10^4	-2.78277×10^5	
	liq	240.5800				
α	ol ^{a)}	2.4661×10^{-5}	9.6809×10^{-9}	1.1503×10^{-3}	-0.4610	
	ol ^{b)}	0.7912×10^{-5}	3.2978×10^{-8}			
	sp	2.1312×10^{-5}	4.4979×10^{-9}		-0.2300	
	liq ^{a)}	9.9499×10^{-5}				
	liq ^{b)}	9.4351×10^{-5}				

Superscript a) denotes that the description of $\alpha\text{-Fe}_2\text{SiO}_4$ (ol) is based on the combination between the thermal expansivity data of Suzuki et al. (1981) and adiabatic bulk modulus data of Sumino (1979), model A. Superscript b) denotes a description based on the thermal expansivity derived from the volume data of Smyth (1975) and adiabatic bulk modulus data of Graham et al. (1988), model B.

adiabatic bulk modulus data of various sources and the quality of the fit resulting from applying model A and B.

The calculated volume-pressure isotherms are compared with the experimental V - P - T data in Table 4 and Figure 6a. From this table and figure it is clear that model A reproduces the experimental data of Plymate and Stout (1990) less than model B. We deduce that systematically higher volumes calculated with model A cannot be explained by non-hydrostatic conditions of the measurements of Plymate and Stout (1990).

4.3. Equation of state parameters for the γ polymorph

For $\gamma\text{-Fe}_2\text{SiO}_4$, adiabatic bulk modulus data ranging between 177 GPa and 212 GPa at room temperature are available from

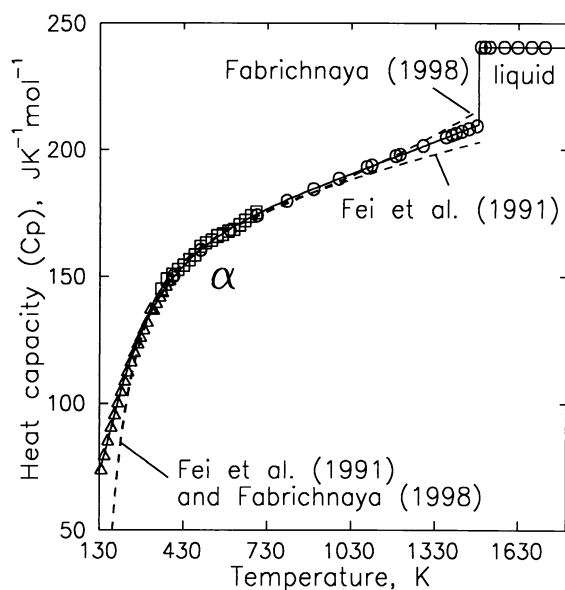


Fig. 1. Polynomial fit of the heat capacity (C_p) at 1 bar pressure of $\alpha\text{-Fe}_2\text{SiO}_4$ together with experimental datapoints of \circ Orr (1953) including liquid, Δ Robie et al. (1982); \square Watanabe (1982). Dashed curves: calculated heat capacity resulting from databases of Fei et al. (1991) and Fabrichnaya (1998). The calculated heat capacity curve resulting from the database of Saxena et al. (1993) has been left out for clarity. It is close to that resulting from the database of Fei et al. (1991).

several sources, see Figure 5. Properties derived from ultrasonic and static compression experiments are given in Tables 1 and 3. Because measurements of the temperature derivative of the bulk modulus are not available, we directed the optimization towards volume-pressure data covering the temperature range between 298 and 1473 K. In the optimization process we allowed the thermal expansivity at 1 bar pressure to vary within the experimental uncertainty as determined by Suzuki et al. (1979). The optimization results in the thermal expansivity function, which is given in Table 2 and plotted in Figure 3. In Table 4 and Figure 7a we compare our results with the volume-temperature data of Mao et al. (1969). The parameters $K^0(T_0)$, $K^0(T_0)$ and α , are listed in Table 5, and give an adiabatic bulk modulus in good agreement with the experimental data, see Table 3 and Figure 5. The pressure derivative $K^0(T_0)$ agrees well with the value 5.0 derived by Liebermann (1975), 5.59 by Rigden and Jackson (1991) and 5.4 ± 2.5 by Plymate and Stout (1994). Table 4 and Figure 6b show the excellent agreement between the calculated volume-pressure isotherms and the experimental data.

5. RESULTS OF PHASE EQUILIBRIA AND CALORIMETRIC DATA

Data on the phase equilibria between the α , γ , and liquid phases of Fe_2SiO_4 are used to reach a consistent description of the Gibbs energy as a function of temperature and pressure for each of these phases. Using the thermophysical, thermochemical and equation of state parameters derived in the preceding section, we derived the enthalpy of formation, absolute entropy and the heat capacity of $\gamma\text{-Fe}_2\text{SiO}_4$ by subjecting calorimetric data and phase diagram data to a thermodynamic analysis. With the results obtained, it becomes possible to derive the equation of state parameters for liquid Fe_2SiO_4 .

5.1. Phase Equilibria Between α - and $\gamma\text{-Fe}_2\text{SiO}_4$

To calculate phase equilibria between the α - and γ forms of Fe_2SiO_4 , the Gibbs energy as a function of temperature and pressure of each form must be established. The Gibbs energy of $\alpha\text{-Fe}_2\text{SiO}_4$ as a function of pressure and temperature has been determined in the preceding section. According to Eqn. (5), the enthalpy of formation, absolute entropy, and heat capacity at 1

Table 3. Summary of the reproducibility of the heat capacity, thermal expansivity, adiabatic bulk modulus and bulk sound velocity data at 1 bar pressure for the three phases of Fe_2SiO_4 .

Property	Maximum absolute deviation in %	Average absolute deviation in %	Temperature range in K	Reference
Heat capacity	0.35	0.13	395–1481	Orr (1953)
α - Fe_2SiO_4	1.56	0.48	136–383	Robie et al. (1982)
	2.24	0.54	350–700	Watanabe (1982)
	0.38	0.20	300–1490	Barin (1989)
Heat capacity	0.91 ^{a)} , 0.78 ^{b)}	0.52 ^{a)} , 0.32 ^{b)}	350–700	Watanabe (1982)
γ - Fe_2SiO_4				
Thermal expansivity	1.45 ^{a)} , 51.94 ^{b)}	0.29 ^{a)} , 21.81 ^{b)}	298–1123	Suzuki et al. (1981)
α - Fe_2SiO_4				
Thermal expansivity	9.97	7.05	273–2273	Suzuki et al. (1979)
γ - Fe_2SiO_4				
Adiabatic bulk modulus	0.49 ^{a)} , 7.76 ^{b)}	0.34 ^{a)} , 7.04 ^{b)}	293–673	Sumino (1979)
	0.81 ^{a)} , 6.24 ^{b)}	0.44 ^{a)} , 5.43 ^{b)}	700–1500	Sumino (1979)
α - Fe_2SiO_4	7.01 ^{a)} , 0.31 ^{b)}	6.82 ^{a)} , 0.17 ^{b)}	273–313	Graham et al. (1988)
Adiabatic bulk modulus	6.77	6.77	298	Mao et al. (1969)
	6.77	6.77	298	Mizutani et al. (1970)
γ - Fe_2SiO_4	2.80	2.80	298	Liebermann (1975)
	0.02	0.02	298	Sato (1977)
	0.52	0.52	298	Finger et al. (1979)
	2.80	2.80	298	Kuskov (1985)
	1.23	1.23	298	Rigden/Jackson (1991)
	4.26	4.26	298	Hazen (1993)
Isothermal bulk modulus	2.63 ^{a)} , 2.13 ^{b)}	1.36 ^{a)} , 1.24 ^{b)}	1503, 1653	Rivers/Carmichael (1987)
liq- Fe_2SiO_4	2.15 ^{a)} , 2.61 ^{b)}	1.47 ^{a)} , 1.96 ^{b)}	1573–1873	Lange/Carmichael (1987)
bulk sound velocity	0.88 ^{a)} , 0.94 ^{b)}	0.58 ^{a)} , 0.60 ^{b)}	1503, 1653	Rivers/Carmichael (1987)
liq- Fe_2SiO_4				

Superscript a) and b) have the same meaning as in Table 2. When no superscript is given, the value applies to both models.

bar pressure of the spinel form in its metastable state must be derived. To this end, we considered experiments determining the phase boundary reported by Akimoto et al. (1965, 1967), obtained with a quench method and X-ray diffraction, Inoue (1975) and Akimoto et al. (1977) both obtained by in situ X-ray diffraction and Yagi et al. (1987), obtained by in situ synchrotron radiation. The phase boundary obtained by Akimoto et al. (1965, 1967) was later revised by Mao et al. (1969) using the NBS pressure scale. In addition we used experimental heat of

transition data of Navrotsky et al. (1979) obtained by solution calorimetric and drop calorimetric measurements from Akaogi et al. (1989).

Yagi et al. (1987) showed that excess pressure is required to initiate the α - γ transition when samples are compressed along an isothermal path. They pointed out that Inoue (1975) determined the phase boundary from the initiation pressure of the olivine-spinel transition in isothermal compression with as result a shift in the phase boundary to higher pressures. These

Table 4. Summary of the fit of the volume data at high pressure for the three forms of Fe_2SiO_4 .

Property	Maximum absolute deviation in %	Average absolute deviation in %	Temperature range in K	Pressure range in GPa	Reference
Volume	0.54 ^{a)} , 0.41 ^{b)}	0.24 ^{a)} , 0.16 ^{b)}	296 \pm 3	0.0–7.3	Yagi et al. (1975)
α - Fe_2SiO_4	0.49 ^{a)} , 0.37 ^{b)}	0.31 ^{a)} , 0.24 ^{b)}	296	0.0–4.2	Hazen (1977)
	1.00 ^{a)} , 0.98 ^{b)}	0.23 ^{b)} , 0.23 ^{b)}	298	0.0–14.0	Kudoh/Takeda (1986)
	0.04 ^{a)} , 0.14 ^{b)}	0.03 ^{a)} , 0.10 ^{b)}	1273	3.9–6.2	Yagi et al. (1987)
	0.54 ^{a)} , 0.30 ^{b)}	0.24 ^{a)} , 0.15 ^{b)}	673	4.6–6.2	Plymate/Stout (1990)
	1.35 ^{a)} , 2.09 ^{b)}	0.72 ^{a)} , 1.10 ^{b)}	300	9.5–37.3	Williams et al. (1990)*
	0.71 ^{a)} , 0.62 ^{b)}	0.32 ^{a)} , 0.28 ^{b)}	298	0.0–10.6	Andraut et al. (1995)
	0.13 ^{a)} , 0.14 ^{b)}	0.07 ^{a)} , 0.05 ^{b)}	298	0.0–9.7	Zhang (1998)
Volume	1.09	0.25	298	0.0–25.5	Mao et al. (1969)
γ - Fe_2SiO_4	0.21	0.07	294–670	0.0	Mao et al. (1969)
	0.06	0.04	298	0.0–4.0	Finger et al. (1979)
	0.31	0.11	773–1473	4.3–6.3	Yagi et al. (1987)
	0.09	0.06	298	0.0–4.8	Hazen (1993)
	1.07	0.48	673	4.5–24.2	Plymate/Stout (1994)
Volume	0.15 ^{a)} , 0.49 ^{b)}	0.10 ^{a)} , 0.27 ^{b)}	1573–1873	0.0	Lange/Carmichael (1987)
liq- Fe_2SiO_4	1.63 ^{a)} , 1.25 ^{b)}	1.55 ^{a)} , 1.21 ^{b)}	1503, 1653	0.0	Shiraishi et al. (1978)

Superscript a) and b) have the same meaning as in Table 2.

* The measurements in this table at high pressure could be carried out due to the metastability of α - Fe_2SiO_4 . Williams et al. (1990) gave the highest pressures for which volume data are present and showed that this form undergoes an amorphisation reaction beyond about 40 GPa.

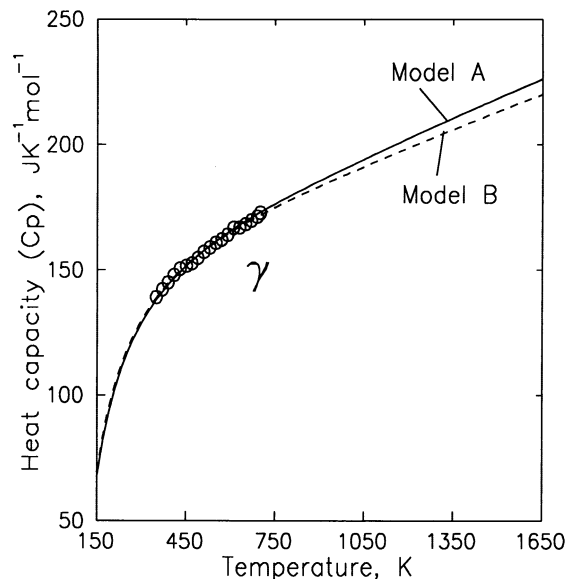


Fig. 2. Polynomial fit of the heat capacity (C_p) at 1 bar pressure of $\gamma\text{-Fe}_2\text{SiO}_4$ together with experimental data of \circ Watanabe (1982). Solid curve: analysis based on model A. Dashed curve: analysis based on model B.

arguments compelled us to direct the optimization towards the experimental phase boundary data of Yagi et al. (1987). The accuracy of their experiments in the temperature range between 1073 K and 1473 K was better than 0.1 GPa and we adopted

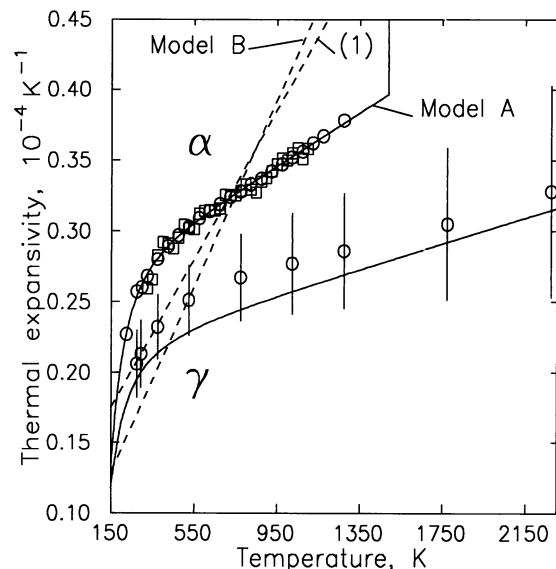


Fig. 3. Polynomial fit of the thermal expansivity of α and $\gamma\text{-Fe}_2\text{SiO}_4$ at 1 bar pressure. $\alpha\text{-Fe}_2\text{SiO}_4$: \square experimental data of Suzuki et al. (1981), \circ fit by Suzuki et al. (1981) using Grüneisen theory. The discontinuity in the calculated curve represents melting. Dashed curve (1) according to Plymate and Stout (1990). $\gamma\text{-Fe}_2\text{SiO}_4$: \circ fit by Suzuki et al. (1979) including error bars using Grüneisen theory based on the experimental V - T data of Mao et al. (1969); data points above $T = 670$ K are extrapolated.

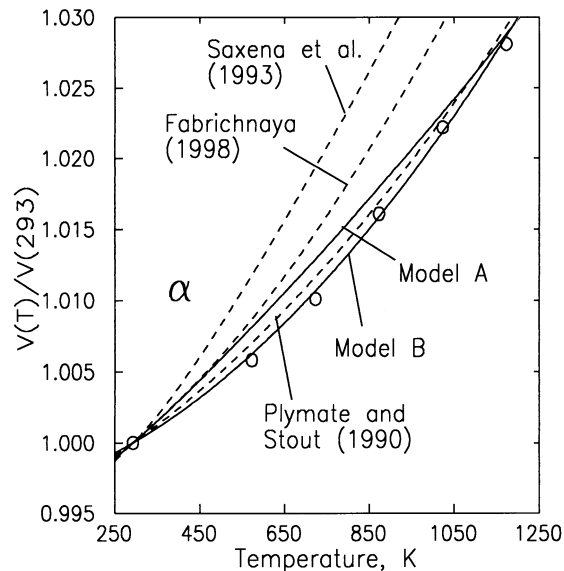


Fig. 4. Calculated volume expansion of $\alpha\text{-Fe}_2\text{SiO}_4$ referred to $T = 293$ K and 1 bar pressure together with experimental data of Smyth (1975). The dashed curve in between the solid curves has been calculated with the expression for the thermal expansivity given by Plymate and Stout (1990). Calculated expansion resulting from databases of Saxena et al. (1993) and Fabrichnaya (1998) are plotted as dashed curves for comparison. The expansion calculated with the database of Fei et al. (1991) coincides with the curve labelled with model A.

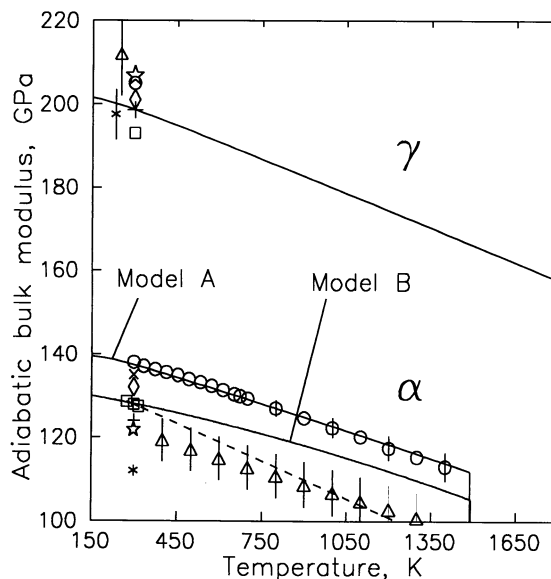


Fig. 5. Calculated adiabatic bulk modulus of α and $\gamma\text{-Fe}_2\text{SiO}_4$ at 1 bar pressure together with experimental data of $\alpha\text{-Fe}_2\text{SiO}_4$: ultrasonic: \ast Mizutani et al. (1970), \ast Chung (1970), \ast Akimoto (1972), \circ Sumino (1979), with points above 673 K extrapolated including error bars, \square Graham et al. (1988), dashed line is extrapolated and height of symbols represents error bars; \triangle Plymate and Stout (1990) with error bars. static compression: \times Takahashi (1970), $+$ Yagi et al. (1975). $\gamma\text{-Fe}_2\text{SiO}_4$: ultrasonic: \triangle Mizutani et al. (1970), \circ Akimoto (1972), \square Liebermann (1975), \diamond Rigden and Jackson (1991); static compression: $+$ Sato (1977), \ast Finger et al. (1979), \ast Hazen (1993). The points of Mizutani et al. (1970) and Finger et al. (1979) are offset to lower temperature for clarity.

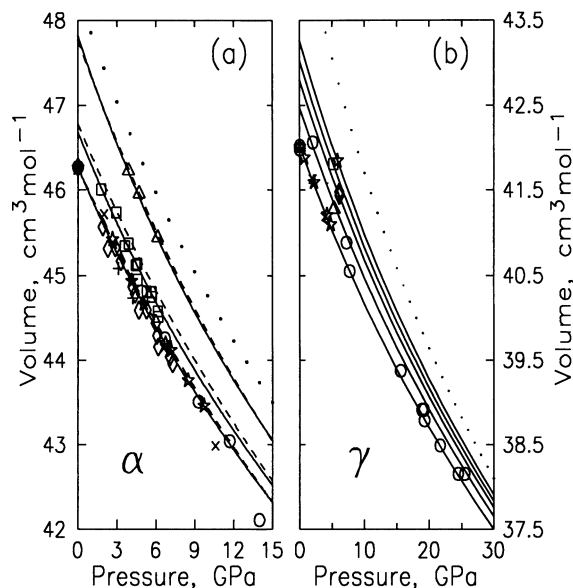


Fig. 6. Calculated compression isotherms of $\alpha\text{-Fe}_2\text{SiO}_4$ and $\gamma\text{-Fe}_2\text{SiO}_4$. $\alpha\text{-Fe}_2\text{SiO}_4$ (a) experimental data of: 298 K: \diamond Yagi et al. (1975), $+$ Hazen (1977), \circ Kudoh and Takeda (1986), \times Andraut et al. (1995), \star Zhang (1998) and 673 K: \square Plymate and Stout (1990) and 1273 K: \triangle Yagi et al. (1987). The dashed curves represent the analysis based on model A and the solid curves represent the analysis based on model B. The dotted curve represents the 1273 K isotherm calculated with the database of Fabrichnaya (1998). $\gamma\text{-Fe}_2\text{SiO}_4$ (b) experimental data at 298 K of: \circ Mao et al. (1969), \times Finger et al. (1979), \star Hazen (1993) and data of Yagi et al. (1987): \triangle 773 K, \diamond 1073 K, \square 1273 K and \star 1473 K. For transparency the 873 K and 1173 K isotherms of Yagi et al. (1987) and the 673 K isotherm of Plymate and Stout (1994) are omitted. The data of the latter investigators are scattered between the 298 K and the 1073 K isotherms. Dotted curve: 1473 K isotherm calculated with the database of Fabrichnaya (1998).

this value as a constraint in our calculations. To take cation disorder into account, we used the value $120.499 \text{ kJ}\cdot\text{mol}^{-1}$ for the interchange enthalpy, based on the structure refinement of Yagi et al. (1974) and the calculation by Navrotsky (1977). Taking the value $119.662 \text{ kJ}\cdot\text{mol}^{-1}$ based on the work of Marumo et al. (1977) and calculation by Navrotsky et al. (1979), has no effect on the curve within 0.008 GPa. The optimization results in a reproduction of the phase boundary data and the transition enthalpy, $\Delta H(\alpha \rightarrow \gamma)$, reported by Navrotsky et al. (1979) and Akaogi et al. (1989) within experimental error limits, see Table 6.

The calculated enthalpy of formation and absolute entropy and expression for the heat capacity are listed in Tables 5 and 2. Values for the transition enthalpy and entropy are given in Table 6 and compared with experimental data. The calculated phase boundary is plotted in Figure 8. It follows from the figure that the phase boundary calculated with model B has a stronger inflection than that calculated with model A. This is caused by the larger change in thermal expansivity with temperature of $\alpha\text{-Fe}_2\text{SiO}_4$ in model B.

5.2. Phase equilibria between α -, γ -, and liquid Fe_2SiO_4

In this section we derive the Gibbs energy formulation of the liquid state using the results for α - and $\gamma\text{-Fe}_2\text{SiO}_4$. Although

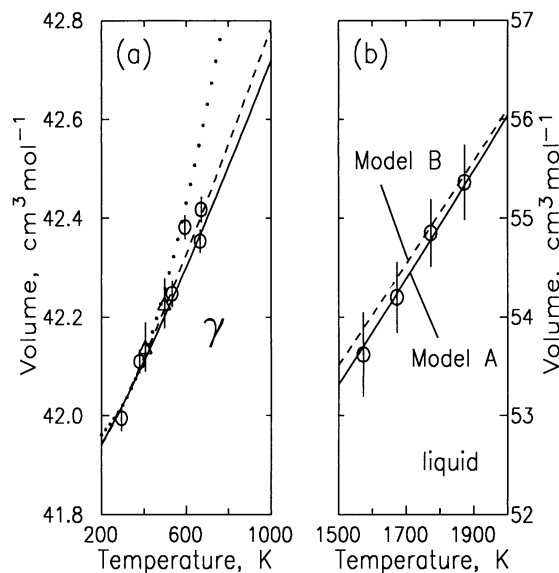


Fig. 7. Calculated volume of $\gamma\text{-Fe}_2\text{SiO}_4$ and liquid at 1 bar pressure. $\gamma\text{-Fe}_2\text{SiO}_4$ (a): experimental data are from Mao et al. (1969): \circ measurements obtained from (440) diffraction line, \triangle obtained from (311) diffraction line. Solid curve: this work, model A and B lead to identical results. Dashed curve: result of Suzuki et al. (1979) and identical with the result calculated with the database of Fei et al. (1991). Dotted curve: result calculated with the database of Saxena et al. (1993) and Fabrichnaya (1998). Liquid Fe_2SiO_4 (b) experimental data are from Lange and Carmichael (1987). Solid curves are calculated with model A. Dashed curves are calculated with model B.

our equation of state is based on a relation derived for and successfully applied to solid substances we tested its validity for liquid materials.

There is a disagreement on the melting behavior of $\alpha\text{-Fe}_2\text{SiO}_4$. Akimoto et al. (1967) and Ohtani (1979), both using microscopy and X-ray analysis, showed that this phase melts congruently up to pressures of ~ 7 GPa. Lindsley (1967) and Hsu (1967) using microscopic examinations and X-ray diffraction observed incongruent melting of $\alpha\text{-Fe}_2\text{SiO}_4$ with the separation of metallic iron. Stebbins and Carmichael (1984) determined that the heat of incongruent melting at the melting temperature is $88.4 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$. They also gave a value of $89.3 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$ for the hypothetical heat of congruent melting, which deviates from $92.174 \text{ kJ}\cdot\text{mol}^{-1}$, as measured by Orr (1953).

With the Gibbs energy functions derived in the preceding sections, we used the phase boundaries for the α -liquid equilibria measured by Akimoto et al. (1967) and the γ -liquid equilibria measured by Ohtani (1979) to construct the Gibbs energy of the liquid phase. Because of uncertainties in the measurements of Ohtani (1979), we allowed a 1 GPa error in the optimization of their γ -liquid phase boundary. In addition we assumed congruent melting of Fe_2SiO_4 . In the optimization, we constrained the enthalpy of formation and absolute entropy of the liquid by taking as the enthalpy of congruent melting $89.3 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$, from Stebbins and Carmichael (1984), and as heat capacity of the liquid $240.58 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from Orr (1953).

In addition we used the ultrasonic measurements of Rivers

Table 5. Thermodynamic properties at 298.15 K and 1 bar pressure. The heat of formation is expressed in $\text{J} \cdot \text{mol}^{-1}$, the absolute entropy in $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, the molar volume in $\text{cm}^3 \cdot \text{mol}^{-1}$, the isothermal and adiabatic bulk modulus in GPa, the pressure derivative of the isothermal bulk modulus being dimensionless. The unit of the equation of state constant a (equation 1) is $\text{m}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. α denotes the olivine and γ the spinel form of Fe_2SiO_4 .

Form	ΔH_f^0	S^0	V^{0*}	$K^0(T_0)$	$a \times 10^{10}$	$K^0 \cdot (T_0)$	$K_S^0(T_0)$
α^a	-1479902	145.197	46.27	136.00 ± 0.63	-4.674 ± 1.434	4.78 ± 0.39	137.33
γ^a	-1474477	133.745	42.02	197.03 ± 2.04	-3.900 ± 0.225	5.09 ± 0.25	198.55
liq ^a	-1460962	95.505	47.30	37.93 ± 4.00	30.200 ± 1.500	11.09 ± 0.80	38.79
α^b	-1479902	145.197	46.27	127.52 ± 0.60	-1.471 ± 1.414	6.14 ± 0.37	128.05
γ^b	-1473948	134.230	42.02	197.03 ± 2.04	-3.900 ± 0.225	5.09 ± 0.25	198.55
liq ^b	-1460962	95.505	47.78	38.11 ± 3.90	29.427 ± 1.500	12.12 ± 0.80	38.89

Superscript a) and b) have the same meaning as in Table 2.

*Volume at 1 bar pressure and 298.15 K for the α and γ form are taken from Jeanloz and Thompson (1983).

and Carmichael (1987), which define the sound speed and isothermal compressibility of the liquid at 1 bar pressure. From the results of Lange and Carmichael (1987), we derived the volume and isothermal compressibility as a function of temperature at 1 bar pressure for liquid Fe_2SiO_4 , in accordance with their deductions of ideal mixing between liquid end member components.

We optimized the thermal expansivity at 1 bar pressure and the equation of state parameters of the liquid. The results are given in Tables 2 and 5 and the phase diagram is plotted in Figure 8. The resulting triple point is located at $(T/K, P/\text{GPa}) = (1810, 6.54)$ for model A and $(1792, 6.26)$ for model B, consistent with the measurements of Ohtani (1979) and Akimoto et al. (1967) respectively. Ohtani (1979) locates this point at $(T/K, P/\text{GPa}) = (1793 \pm 25, 7.0 \pm 0.5)$ and Akimoto (1967) at $(T/K, P/\text{GPa}) = (1793 \pm 20, 6.2 \pm 0.2)$. Table 4 and Figure 7b show that the experimental volume data at 1 bar pressure are well reproduced by model A as well as B. Table 3 and Figure 9 show that the same applies to the experimental isothermal bulk modulus data and bulk sound velocities.

6. DISCUSSION

We divided this section into three parts. In the first part we address the results of the two models A and B, and the use of different equations of state. In the second part we discuss differences in thermochemical and thermophysical properties when applying various databases given in the literature. In the

last part we combine the results we found for Mg_2SiO_4 (Jacobs and Oonk, 2001b) with our present results or results stemming from existing databases. In this last part we also discuss the implications for isotropic (bulk) sound wave velocities in the earth's upper mantle.

6.1. Results of the Models A and B and Equations of State

The calculated value for the pressure derivative $K^{0'}(T_0)$ of 4.78 ± 0.39 , given in Table 5, obtained with model A compares well with the experimentally obtained values 5.0 ± 1.0 (Sumino, 1979), 5.2 ± 0.4 (Graham et al., 1988) and 4.1 ± 0.7 (Zhang, 1998). The calculated value $K^{0'}(T_0) = 6.14 \pm 0.37$ obtained with model B seems too high though it compares well with the value 6.5 ± 2.0 derived by Plymate and Stout (1990).

Figure 5 demonstrates that the slope $(\partial K_S/\partial T)_P$ calculated with model B is less negative than that determined by Graham et al. (1988) and Sumino (1979). Fixing the slope of the adiabatic bulk modulus curve to the value given by Graham et al. (1988) has an effect that the calculated volumes at 1273 K are too low compared with those determined by Yagi et al. (1987). The effect of a more negative slope $(\partial K_S/\partial T)_P$ may also be demonstrated by considering the calculations of Plymate and Stout (1990). They optimized all V - P - T data, except those of Zhang (1998), with a temperature corrected Murnaghan equation of state. To reproduce the data a thermal expansivity

Table 6. Comparison of the calculated transition enthalpy (in $\text{J} \cdot \text{mol}^{-1}$) and transition entropy (in $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) for the transition $\alpha \rightarrow \gamma$ at 1 bar pressure with experimental data.

T/K	ΔH	ΔS	Reference
298	6610 ± 2430		Akaogi et al. (1989)
	5425 ± 1000	-11.451 ± 0.90	Calculated ^{a)}
	5954 ± 700	-10.968 ± 0.59	Calculated ^{b)}
	6670	-9.966	Fei et al. (1991)
	6670	-9.966	Saxena et al. (1993)
986	12275	-5.172	Fabrichnaya (1998)
	2941 ± 828	-19.974 ± 0.84	Navrotsky et al. (1979)
		-17.57 ± 0.84	Navrotsky/Akaogi (1984)
	3769 ± 900	-15.135 ± 0.90	Calculated ^{a)}
	3769 ± 700	-15.141 ± 0.59	Calculated ^{b)}
	4704	-14.103	Fei et al. (1991)
	5497	-12.309	Saxena et al. (1993)
	10899	-8.241	Fabrichnaya (1998)

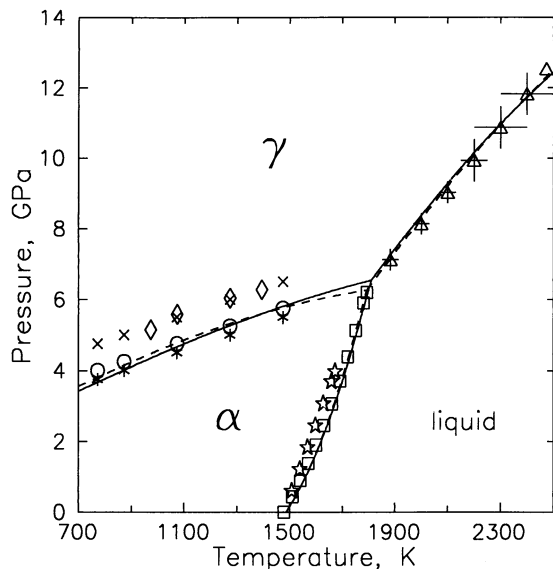


Fig. 8. Phase diagram of the system Fe_2SiO_4 with experimental data. α - γ boundary: * Akimoto et al. (1965, 1967) revised by Mao et al. (1969), \diamond Akimoto et al. (1977), \circ Yagi et al. (1987) with points below 1073 K extrapolated and \times Inoue (1975). α -liquid boundary: \square Akimoto et al. (1967), \star Hsu (1967). γ -liquid boundary: \triangle Ohtani (1979). Solid curves are calculated with model A. Dashed curves are calculated with model B.

function at 1 bar pressure was introduced which deviates from that of Suzuki et al. (1981), see Figure 3, as well as to some extent from the data of Smyth (1975), see Figure 4. Their calculated slope of the adiabatic bulk modulus is more negative

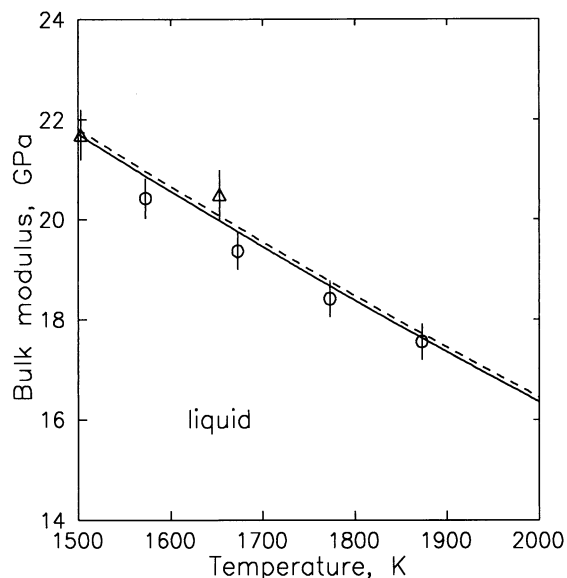


Fig. 9. Calculated isothermal bulk modulus of liquid Fe_2SiO_4 at 1 bar pressure together with experimental data of \triangle Rivers and Carmichael (1987) and \circ Lange and Carmichael (1987). Solid curves are calculated with model A. Dashed curves are calculated with model B.

than ours is and the calculated 1273 K isotherm lays below the experimental data of Yagi et al. (1987).

Both models A and B properly describe the calorimetric data of Navrotsky et al. (1979), of Akaogi et al. (1989), and the phase boundary data of Yagi et al. (1987). The quality of fit of the phase boundary data obtained with model B improved relative to that of model A. The mean deviation between calculation and experiment is 0.08 GPa for model A and 0.04 GPa for model B.

The application of a Murnaghan, Birch-Murnaghan, or Universal equation of state does not improve our thermophysical results for α - and γ - Fe_2SiO_4 . These results, given in Table 2 and 5, can be used as input in these equations of state. A four-parameter polynomial fit of the isothermal compressibility of the two solid forms and liquid is given in Table 7. All experimental data are reproduced with an accuracy similar to that resulting from our equation of state. A characteristic of employing a Murnaghan, Birch-Murnaghan or a Universal equation of state is that the thermal expansivity attains negative values at temperatures around 300 K and pressures of ~ 40 GPa, which is approximately the maximum pressure at which Williams et al. (1990) report volume data.

As outlined in section 5.2, both models A and B suit the description of the liquid phase when the constraint of congruent melting is imposed. The assessment of the equilibria involving liquid is complicated by the fact that Ohtani (1979) corrected the measurements below 10 GPa on the basis of the α - γ Fe_2SiO_4 transition curve reported by Akimoto et al. (1977). This correction is ~ 1 GPa higher than that reported by Yagi et al. (1987), which we used in our description. It comes as a surprise that even with a 1 GPa variation in the γ -liquid boundary, the data of Ohtani (1979) are reproduced well.

Using models A and B, the volume data and isothermal bulk modulus data of Lange and Carmichael (1987) for liquid Fe_2SiO_4 are reproduced well. This also applies to the isothermal bulk modulus data and bulk sound velocity data of Rivers and Carmichael (1987). The absolute value for the constant a for liquid is larger than that for the solid forms. As a consequence the values given in Tables 2 and 5 for the liquid form cannot be used in other equations of state without loss of accuracy in the description of the experimental data. In Table 7 we give the results of the data optimization for the liquid form using several equations of state. The experimental data are described with similar accuracy as when using our equation of state. Table 7 clearly indicates that application of a Birch-Murnaghan equation of state results in a higher value for the pressure derivative $K^0(T_0)$ compared to a Murnaghan or Universal equation of state. Comparing the results given in Table 5 for the liquid form with those given in Table 7 indicate that the calculated properties resulting from our equation of state are close to those resulting from a Murnaghan equation of state.

6.2. Comparison with results from other databases

In this section we compare our results of thermochemical and thermophysical properties with results calculated from databases of Fei et al. (1991), Saxena et al. (1993), and Fabrichnaya (1998). In Figure 1 we plotted the heat capacity of α - Fe_2SiO_4 . Our results give a more accurate representation of the data in a larger temperature range. The heat capacity data of

Table 7. Calculated isothermal compressibility (in Pa^{-1}), $\kappa = k_1 + k_2 * T + k_3 * T^2 + k_4 * T^3$. The results are obtained by fitting the calculated isothermal compressibility in the temperature range 150–2500 K, resulting from Eqns. (1) and (2) together with the values given in Table 5. For liquid, the isothermal compressibility, thermal expansivity α , pressure derivative and volume $V^0(T_0)$ at 1 bar and 298.15 K have been optimized.

Form	$k_1 \times 10^{12}$ (Pa^{-1})	$k_2 \times 10^{15}$ ($\text{Pa}^{-1} \cdot \text{K}^{-1}$)	$k_3 \times 10^{19}$ ($\text{Pa}^{-1} \cdot \text{K}^{-2}$)	$k_4 \times 10^{23}$ ($\text{Pa}^{-1} \cdot \text{K}^{-3}$)	$\alpha \times 10^4$ (K^{-1})	$K^{0'}$ (T_0)	$V^0(T_0)$ (cm^3)
α	6.9853 ^{a)}	1.1803	2.1253	7.8741			
	7.5016 ^{b)}	1.1515	-1.6001	52.7621			
γ	4.8582	0.6942	1.3840	1.6303			
liq							
BM	24.2595 ^{a)}	12.5494	-20.3813	270.0161	1.18 ± 0.10	16.47 ± 4.00	46.06 ± 0.45
MUR	22.9208	12.5494	-20.3813	270.0161	1.03 ± 0.10	12.42 ± 1.43	47.05 ± 0.45
UNI	23.8337	12.5494	-20.3813	270.0161	1.12 ± 0.10	13.78 ± 2.50	46.47 ± 0.45
BM	23.4472 ^{b)}	12.4212	-19.0192	263.2562	1.10 ± 0.08	19.86 ± 3.81	46.59 ± 0.42
MUR	22.8299	12.4212	-19.0192	263.2562	0.99 ± 0.10	13.18 ± 1.36	47.49 ± 0.42
UNI	23.2488	12.4212	-19.0192	263.2562	1.05 ± 0.10	14.98 ± 2.30	47.03 ± 0.45

Superscript a) and b) have the same meaning as in Table 2. For liquid the results in Table 5 serve as input in either a Murnaghan (MUR), Birch-Murnaghan (BM) or Universal (UNI), see Vinet et al. (1987), equation of state. For the α and γ form the values are valid for all equations of state.

Watanabe (1982) for $\gamma\text{-Fe}_2\text{SiO}_4$ are represented equally well by all databases. Table 6 shows that the experimental enthalpy change for the transition of the α to the γ form is best represented by models A and B. In contrast to our database, the other databases lead to some deviation with respect to the experimental data of Navrotsky et al. (1979). According to Fabrichnaya (1998), high values for the transition enthalpy are necessary to reach agreement in the description of the complex behavior of phase equilibria in the Fe-Si-O system. Although we may be faced in the future with the difficulties she points out, we wanted to achieve here a thermodynamic description which describes as closely as possible the experimental data available for Fe_2SiO_4 , empowering us to pinpoint inconsistencies in experimental data in more complex systems.

Turning first to volume expansion, Figure 4 indicates that the volume expansion at 1 bar pressure of $\alpha\text{-Fe}_2\text{SiO}_4$ calculated with the databases of Saxena et al. (1993) and Fabrichnaya (1998) deviates from the experimental data of Smyth (1975) and Suzuki et al. (1981). These deviations result from the aforementioned problem to reach consistency of phase equilibria in the Fe-Si-O system. The application of the database of Fei et al. (1991) results in a volume expansion identical with that of Suzuki et al. (1981) and used in our model A. Because of the deviations depicted in Figure 4, the databases of Saxena et al. (1993) and Fabrichnaya (1998) lead to deviations in the description of the volume-pressure-temperature data given in Figure 6a. Considering these two databases, only the one of Fabrichnaya results in a description of the 298 K and 673 K isotherm with an accuracy comparable to our model A. On the other hand the database of Fei et al. (1991) leads to similar accuracy with our model A for all three experimentally measured isotherms.

Turning to the bulk modulus, the adiabatic bulk modulus of $\alpha\text{-Fe}_2\text{SiO}_4$ calculated from the databases of Fei et al. (1991) and Saxena et al. (1993) represents the experimental data of Sumino (1979) with an accuracy similar to our model A. The database of Fabrichnaya (1998) results in an adiabatic bulk modulus representing the data of Graham et al. (1988) in the temperature range between 273 K and 313 K and the extrapolated data of Sumino (1979) at temperatures higher than 1000 K.

Figure 7a shows that the volume expansion at 1 bar pressure of $\gamma\text{-Fe}_2\text{SiO}_4$ is well described by using the database of Fei et al. (1991). It is identical with the description of Suzuki et al. (1979). The resulting volume expansion from the databases of Saxena et al. (1993) and Fabrichnaya (1998) is identical and deviates from the experimental data at higher temperatures. The database of Fei et al. (1991) leads to a comparable description of the V - P - T data, depicted in Figure 6b, as our models A and B for pressures smaller than 10 GPa. The calculated 298 K isotherm at pressures higher than 10 GPa is lower than the experimental data of Mao et al. (1969) and deviates from our description. The isotherms calculated with the databases of Saxena (1993) and Fabrichnaya (1998) deviate from the experimental data used in Figure 6b. Comparing the results extracted from the three databases with ours, we come to the conclusion that our Gibbs energy formulation of the α and γ forms leads to an improvement of the representation of all considered experimental data.

6.3. Implications for bulk sound velocities

Results of thermophysical data may deviate substantially between different databases. Here we want to discuss what the effect is of these variations on the bulk sound velocity, a property that results directly from thermodynamic analysis. Figure 10 depicts calculated bulk sound velocities as a function of pressure at 1500 K for $\alpha\text{-Fe}_2\text{SiO}_4$ calculated with our models A and B and those resulting from other databases. At pressures and temperatures prevailing at around the 400 km seismic discontinuity, 13 GPa and 1500 K, the differences in velocity for $\alpha\text{-Fe}_2\text{SiO}_4$ are substantial, varying between 0.2 and 0.6 km/s. Such differences fall within the detection limit of seismic experiments.

In the preceding section we noted that the difference between volume as function of pressure and temperature calculated with model A and that calculated with the database of Saxena et al. (1993) is quite large. The results calculated with model A and with the database of Fei et al. (1991) differ less. From Figure 10 we note however that this trend is not the case for bulk sound velocities, the reason being that bulk sound velocity is the square root ratio of adiabatic bulk modulus and density.

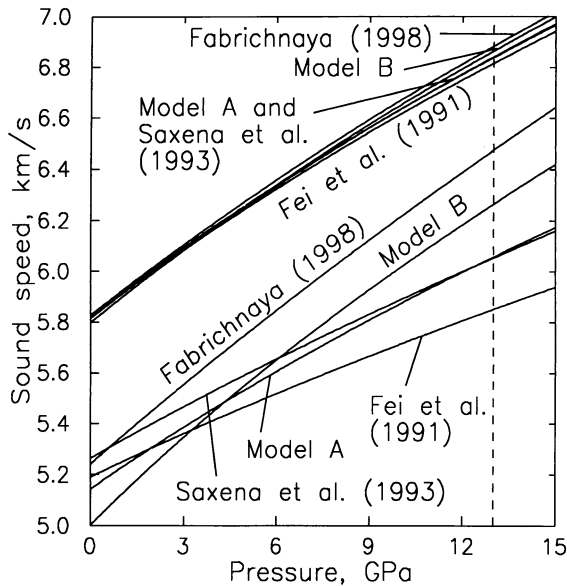


Fig. 10. Bulk sound velocity as a function of pressure at 1500 K for $\alpha\text{-Fe}_2\text{SiO}_4$ (lower part) and $\alpha\text{-(Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ (upper part, curves entirely above 5.8 km/s). Dashed line indicates conditions around 400 km depth in the earth. Calculations are made with models A and B, and with the databases of Fei et al. (1991), Saxena et al. (1993), and Fabrichnaya (1998).

Because we are mainly interested in the behavior of thermochemical and thermophysical properties of mantle materials, we combined our recent results of Mg_2SiO_4 (Jacobs and Oonk, 2001b), with the results presented here. We perform the same exercise as the above one for a $\alpha\text{-(Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ solid solution. This mixture approaches a pyrolitic composition in which CaO , Al_2O_3 , alkali oxides and some other oxides are neglected (Ringwood, 1990). Neglecting excess volume, we compare our results obtained with models A and B with those obtained with other databases in Figure 10. Introducing excess volume, which can be calculated from the experimental data of Fisher and Medaris (1969), does not affect the curves. From the figure it is seen that the trends propagate to higher Mg composition and that the differences in bulk sound velocity calculated using the various databases become small. At 13 GPa and 1500 K, the largest difference, 0.06 km/s, is found for results obtained with the databases of Fei et al. (1991) and Fabrichnaya (1998). The differences in bulk sound velocity are reduced with a factor 10 compared with $\alpha\text{-Fe}_2\text{SiO}_4$. Repeating the calculations for the γ form we find that maximum bulk sound velocity differences of ~ 0.4 km/s in $\gamma\text{-Fe}_2\text{SiO}_4$ are reduced to 0.05 km/s in $\gamma\text{-(Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$. We infer from this that sound velocities are not strong discriminators in selecting Gibbs energy formulations for Fe_2SiO_4 using one database versus another, in contrast to what we found for Mg_2SiO_4 , Jacobs and Oonk (2001b).

7. CONCLUSIONS

A thermodynamically consistent Gibbs energy formulation of the α , γ , and liquid forms of Fe_2SiO_4 has been established using Grover, Getting, and Kennedy's empirical relationship between volume and logarithm of the isothermal bulk modulus.

Because the pressure range (0–13 GPa) is small compared with pressures prevailing in the earth's mantle, the results for the solid forms can be used as input for e.g., a Murnaghan or a Birch-Murnaghan equation of state without significant loss of accuracy in the reproduction of all experimental data. Our equation of state has as advantage that a smaller number of parameters must be optimized. Applying our equation of state we optimized three parameters $K^0(T_0)$, a , and b . To reach the same degree of accuracy to reproduce the experimental data applying other equations of state we used four parameters for the isothermal bulk modulus, $K^0(T)$, and additionally one parameter for its pressure derivative, $K^0(T_0)$.

We conclude that the thermal expansivity derived from the volume-temperature data of Smyth (1975) and the adiabatic bulk modulus data of Graham et al. (1988) for $\alpha\text{-Fe}_2\text{SiO}_4$ (model B) lead to the most accurate reproduction of all experimental data considered here. As a consequence, the behavior of the thermal expansivity of the α and γ forms at 1 bar pressure with temperature is different from what we found in the system Mg_2SiO_4 , Jacobs and Oonk (2001b).

The experimental data for liquid Fe_2SiO_4 are not accurate enough to constrain further the thermochemical and thermophysical properties of the solid forms. Within the accuracy of experimental data for the liquid, it is possible to assume congruent melting of Fe_2SiO_4 .

Thermochemical and thermophysical properties of Fe_2SiO_4 calculated with various databases may differ substantially from our results.

For $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$ solid solutions around a pyrolitic composition, we conclude that bulk sound velocity is not a strong discriminator in selecting Gibbs energy formulations for Fe_2SiO_4 using one database versus another. This is in contrast to what we found for Mg_2SiO_4 , Jacobs and Oonk (2001b).

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