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Determination of the partial molar volume of SiO₂ in silicate liquids at elevated pressures and temperatures: A new experimental approach

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Abstract—This study presents a new approach for determining the partial molar volume and its pressure derivative for a silicate liquid component through an experimental determination of the isothermal pressure dependence of the solubility in the liquid of a crystalline phase having the composition of the component. Because this approach allows the determination of partial molar volumes of liquid components at elevated pressure, it has the potential to detect pressure-induced structural changes associated with particular components in silicate liquid through their influence on partial molar volumes. To illustrate the approach, an experimental determination of the solubility of quartz in a rhyolitic liquid was used to determine the partial molar volume of SiO₂ at pressures up to 35 kbar and a temperature of 1350°C. The 1 bar partial molar volume for SiO₂ determined in this way, 2.635 ± 0.009 J/bar, is slightly smaller than the 2.690 ± 0.006 J/bar determined by Lange and Carmichael (1987) (all uncertainties are 1σ). The isothermal pressure dependence of the partial molar volume of SiO₂ at 10 to 35 kbar ($-8.69 \times 10^{-6} \pm 6.1 \times 10^{-7}$ J/bar²) is approximately one-half of the value determined by Kress and Carmichael (1991) at 1 bar ($-1.96 \times 10^{-5} \pm 0.2 \times 10^{-6}$ J/bar²). Our high pressure determination can be reconciled with the existing 1 bar volume and compressibility data if the isothermal pressure dependence of the partial molar volume of SiO₂ in silicate liquids decreases rapidly between 1 bar and 10 kbar, then remains approximately constant to at least 35 kbar. Copyright © 1998 Elsevier Science Ltd

1. INTRODUCTION

Experimental determinations of the physical properties of silicate liquids place constraints on the rates of buoyancy-driven melt segregation (Stolper et al., 1981; Delano, 1990; Circone and Agee, 1996), on the structure of silicate liquids (Bottinga and Weill, 1972; Kushiro, 1976; Rigden et al., 1988, 1989), and on the nature of crystal-liquid differentiation processes (Walker and Hays, 1977; Nisbet and Walker, 1982; Agee and Walker, 1988a, b, 1993). Available experimental data on the density and compressibility of silicate liquids comprise primarily high-temperature partial molar volume and compressibility determinations carried out at 1 bar, supplemented by limited measurements made at higher pressures (Bottinga and Weill, 1970; Kushiro, 1978; Nelson and Carmichael, 1979; Mo et al., 1982; Lange and Carmichael, 1987; Rivers and Carmichael, 1987; Dingwell and Brearley, 1988; Dingwell et al., 1988; Rigden et al., 1988, 1989; Agee and Walker, 1988b, 1989; Kress and Carmichael, 1991; Webb et al., 1992; Agee, 1992a, b; Agee and Walker, 1993; Knoche et al., 1995; Circone and Agee, 1996; Dingwell et al., 1996). Although, in principle, density measurements on liquids covering the appropriate compositional range could be used to derive the partial molar volumes of oxide components at elevated pressures, in practice such information is not currently available.

Here we describe a new approach to determining the partial molar volumes of silicate-liquid components at elevated

pressures and temperatures. The data acquired using this approach represent an important complement to existing 1 bar data. Because the approach is based on an experimental determination of the liquid composition, the data can, in principle, be used to identify pressure-induced changes in liquid structure without introducing the potential complications commonly associated with quenching or the glass transition (Kushiro et al., 1976; Kushiro, 1978; Stolper and Ahrens, 1987; Brandiss and Stebbins, 1988; Rigden et al., 1988, 1989; Williams and Jeanloz, 1988). The approach is based on the fact that the pressure derivative of the chemical potential of a component in a phase is equal to its partial molar volume. Using SiO₂ as an example, in this study we determined by experiment the pressure dependence of the solubility of quartz in a rhyolitic liquid at 1350°C. It was then possible to derive the partial molar volume of SiO₂ in these quartz-saturated liquids as a function of pressure given (1) knowledge of the chemical potential of SiO₂ in the liquids at 1 bar as a function of composition, (2) that the chemical potential of SiO₂ in the experimentally produced, quartz-saturated liquids can be determined given knowledge of the thermochemistry and equation of state of the coexisting quartz, and (3) the assumption, validated at 1 bar (Bottinga and Weill, 1970; Lange and Carmichael, 1987; Knoche et al., 1995), that the partial molar volume of SiO₂ in the liquid is independent of composition over the range of quartz-saturated compositions produced in the experiments. This approach is equally applicable to other liquid components (e.g., corundum for Al₂O₃; rutile for TiO₂; hematite for Fe₂O₃; forsterite for Mg₂SiO₄; etc.) and has promise to provide accurate and precise information on partial molar volumes of oxide and mineral components in silicate liquids at high temperatures and pressures.

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2. THEORY

The background to our approach is as follows. The chemical potential of SiO_2 in liquid of a given composition at pressure, P , and temperature, T , ($\mu_{\text{SiO}_2}^{\text{liq}}(P,T,X)$) is given by:

$$\mu_{\text{SiO}_2}^{\text{liq}}(P,T,X) = \mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar},T,X) + \int_{1 \text{ bar}}^P \bar{V}_{\text{SiO}_2}^{\text{liq}}(P,T)dP \quad (1)$$

where $\mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar},T,X)$ is the chemical potential of SiO_2 in a liquid of the same composition at 1 bar and $\bar{V}_{\text{SiO}_2}^{\text{liq}}(P,T)$ is the partial molar volume of SiO_2 in this same liquid. For a liquid saturated with β -quartz:

$$\mu_{\text{SiO}_2}^{\text{liq}}(P,T,X) = \mu_{\text{SiO}_2}^{\beta\text{Qtz}}(P,T). \quad (2)$$

Substituting Eqn. 2 into Eqn. 1 and rearranging:

$$\int_{1 \text{ bar}}^P \bar{V}_{\text{SiO}_2}^{\text{liq}}(P,T)dP = \mu_{\text{SiO}_2}^{\beta\text{Qtz}}(P,T) - \mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar},T,X) \equiv \Delta\mu_{\text{SiO}_2}. \quad (3)$$

Differentiating both sides of Eqn. 3 with respect to pressure at constant temperature and liquid composition, we arrive at an expression for the partial molar volume of SiO_2 in the liquid that requires a knowledge only of the thermochemistry and equation of state of quartz and the chemical potential of SiO_2 in the liquid at 1 bar:

$$\bar{V}_{\text{SiO}_2}^{\text{liq}} = \left. \frac{\partial(\mu_{\text{SiO}_2}^{\beta\text{Qtz}}(P,T) - \mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar},T,X))}{\partial P} \right|_{T,X} = \left. \frac{\partial\Delta\mu_{\text{SiO}_2}}{\partial P} \right|_{T,X}. \quad (4)$$

Assuming that $\bar{V}_{\text{SiO}_2}^{\text{liq}}$ is independent of liquid composition, once the compositions of liquids saturated with β -quartz are determined experimentally over a range of pressures at a single temperature, the partial molar volume of SiO_2 in the liquid can be calculated as a function of pressure from the relationships given by Eqns. 3 or 4. Compilations such as that of Berman (1988) can be used to calculate $\mu_{\text{SiO}_2}^{\beta\text{-Qtz}}(P,T)$ for each experiment. Note that this also provides the chemical potential of SiO_2 in the quartz-saturated liquid at the experimental pressure and temperature ($\mu_{\text{SiO}_2}^{\text{liq}}(P,T,X)$). However, if a liquid of the same composition is then considered at a pressure of 1 bar and the temperature of interest, it will be undersaturated with respect to a crystalline SiO_2 polymorph. Consequently, the chemical potential of SiO_2 in this liquid at 1 bar ($\mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar},T,X)$) cannot be calculated from thermochemical data for a crystalline phase, but it can be calculated using one of the available solution models for silicate liquids (e.g., Ghiorso and Sack, 1995) or determined experimentally using Pd-oxide equilibration (Chamberlin et al., 1994). Once a $\Delta\mu_{\text{SiO}_2}$ value has been calculated for each of a series of experiments carried out over a range of pressures, a functional form for the pressure dependence of $\Delta\mu_{\text{SiO}_2}$ is assumed (e.g., a polynomial or an integrated form of the Birch-Murnaghan equation of state) and the coefficients in this expression are determined by least squares regression or a nonlinear fitting technique; $\bar{V}_{\text{SiO}_2}^{\text{liq}}$ is then determined by differentiating the resulting expression with respect to pressure.

Note that this approach need not be limited to oxide components or to phases without solid solution. For example, in principle, it could be used to determine partial molar volumes of silicate mineral components (e.g., the Mg_2SiO_4 component in olivine-saturated liquids), although if the component of interest is present in the saturating crystalline phase as a solid solution, a solution model describing the mixing properties of the crystalline phase is needed to extract the components partial molar volume in the liquid phase.

3. EXPERIMENTAL AND ANALYTICAL METHODS

3.1. Starting Materials

Starting materials for the experiments consisted of fresh, clean pieces of natural, high- SiO_2 rhyolitic obsidian from Glass Buttes, Oregon, USA, that had been powdered in a WC shatterbox, and Johnson-Matthey® high-purity (99.999%) amorphous SiO_2 powder. Experiments were performed using either rhyolite powder or a mixture of rhyolite and amorphous SiO_2 prepared by weighing out each powder and grinding the mixture under ethanol for 30 min with an agate mortar and pestle (Table 1). The bulk composition of the rhyolite was determined by first melting 10 mg of rock powder at 10 kbar and 1500°C using the experimental techniques described below; the composition of the resulting glass was then determined by electron microprobe analysis (Table 2). A chip of the natural rhyolitic glass was analyzed by FTIR spectroscopy and its H_2O content was determined to be 0.13 wt%.

3.2. Experimental Methods

Experiments were conducted at 10 to 35 kbar using a 1.27 cm solid-medium piston-cylinder device (Boyd and England, 1960). 4–10 mg of rhyolite \pm amorphous SiO_2 powder were loaded into a graphite crucible and then placed into a Pt capsule that was open at one end. Graphite powder was packed on top of the crucible, the Pt capsule was crimped shut, and the assembly was dried at 400°C for 2 to 6 h. The Pt capsule was then welded shut and centered in a straight-walled graphite furnace using crushable MgO spacers that had been dried at 1000°C for 14 to 138 h. The pressure medium consisted of a CaF_2 sleeve.

Pressure was applied using the cold piston-in technique (Johannes et al., 1971). The friction correction associated with our experimental assembly at 12 to 14 kbar and 1300°C was determined to be <1 kbar through calibration against the Ca-Tschermakite breakdown reaction (Hays, 1966), and no correction has been applied to the pressures reported in Table 1. Temperature was measured and controlled using a $\text{W}_3\text{Re}_{97}/\text{W}_{25}\text{Re}_{75}$ thermocouple, and no correction for the effect of pressure on thermocouple EMF has been applied to the temperatures reported in Table 1. Thermocouple oxidation over the course of an experiment was minimized by flowing N_2 gas over the thermocouple wires. Temperatures are estimated to be accurate to ± 5 to 10°C and pressures to ± 0.5 kbar, and the thermal gradient over the capsule is $<5^\circ\text{C}$ (Baker and Stolper, 1994). Experiments were terminated by shutting off the power.

An experiment was also conducted at 1 bar in a Deltech vertical quenching furnace. 75 mg of rhyolite + amorphous SiO_2 powder were packed into a Pt capsule 1.27 cm in length. The top of the capsule was crimped shut, the assembly was dried for 4 h at 400°C, then the capsule was welded shut. The capsule was suspended in the furnace hot spot for 120 h, then quenched into deionized H_2O . Temperature was continuously monitored using a Pt-Pt₉₀Rh₁₀ thermocouple and is estimated to be accurate to $\pm 3^\circ\text{C}$.

3.3. Analytical Methods

The compositions of experimentally produced silicate glasses were analyzed using the 5-spectrometer JEOL 733 electron microprobe at the California Institute of Technology. The accelerating voltage was 15

TABLE 1. Experimental conditions, starting mixtures, and phase proportions.

Experiment	P (kbar)	Temperature (°C)	Duration (hr)	SiO ₂ ¹ (wt%)	Phase Proportions (wt%) ²	
					Liquid	Crystal
Synthesis Experiments						
GBR-26	0.001	1350	120	50	78.0±1.4	22.0±1.2
GBR-3	10	1350	24	30	87.7±0.6	12.3±0.5
GBR-5	15	1350	24	30	69.3±0.5	30.7±0.4
GBR-2	20	1350	24	30	63.1±0.4	36.9±0.3
GBR-6	25	1350	24	30	59.4±0.5	40.6±0.4
GBR-11	30	1350	24	0	78.9±0.6	21.1±0.4
GBR-10	35	1350	24	0	77.6±0.5	22.4±0.3
Reversal and Variable Duration Experiments						
GBR-14	15	1450	24	30		
	15	1350	24		70.2±0.4	29.8±0.3
GBR-15	15	1450	24	30	75.5±0.5	24.5±0.4
GBR-17	15	1350	3	30	68.1±0.5	31.9±0.4
GBR-12	15	1350	8	30	67.8±0.3	32.2±0.2
GBR-18	15	1350	48	30	70.0±0.3	30.0±0.3
GBR-19	15	1350	72	30	69.6±0.4	30.4±0.3

¹Percentage of amorphous SiO₂ included in starting material by weight. For example, 30 means that the starting mixture consisted of 70% Glass Buttes Rhyolite + 30% amorphous SiO₂ by weight.

²Phase proportions were calculated using unweighted materials balance. Stated uncertainties are 1 σ .

kV, and the beam current was 2.5 nA. Data were reduced using a modified ZAF procedure (Armstrong, 1988). During each analytical session, one spectrometer was dedicated to counting only Si X-rays to minimize the uncertainty associated with reproducibility of the spectrometer position relative to the Si peak (Hanson et al., 1996). A low beam current (2.5 nA) and a 5 to 10 μm^2 raster were used to ensure that the measured abundance of SiO₂ was not influenced by the migration of Na from the excitation volume during the course of an analysis (Si “grow-in”) (Morgan and London, 1996). Sodium and silicon counts collected on the natural obsidian starting material for varying durations (1 to 60 s) demonstrate that these analytical conditions lead to minimal migration of Na from the excitation volume. The precision and reproducibility of the analyses were assessed by analyzing a chip of the natural obsidian starting material 11 to 25 times at the beginning of

each analytical session. On the basis of standard deviations calculated from the distribution of 129 replicate analyses collected over a 15 month period, the relative analytical uncertainties (1 σ) associated with the major oxides are 0.49% for SiO₂, 1.75% for Al₂O₃, 4.20% for Na₂O, and 3.38% for K₂O. The low beam current and relatively short counting times used to minimize Na migration resulted in significant analytical uncertainties for the minor elements (TiO₂, Cr₂O₃, MnO, MgO). The SiO₂ polymorph present in the high-pressure experiments was confirmed to be α -quartz on the basis of powder X-ray diffraction measurements performed on several of the run products (GBR-6, -10, -11). It is assumed that the stable polymorph at experimental conditions was β -quartz. The SiO₂ polymorph in the 1 bar experiment (GBR-26) was determined to be cristobalite, which is metastable at the conditions of this experiment.

TABLE 2. Electron microprobe analyses of experimentally produced silicate liquids.

Experiment	P (kbar)	Analyses	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total
Starting Composition ¹													
		25	77.2(3)	0.01(3)	12.4(2)	0.04(3)	0.71(7)	0.07(4)	0.06(2)	0.50(5)	4.2(2)	4.19(8)	99.38
Synthesis Experiments													
GBR-26	0.001	20	85.2(4)	0.09(10)	7.7(2)	0.05(4)	0.48(9)	0.04(5)	0.05(3)	0.32(5)	2.44(16)	2.56(8)	98.93
GBR-3	10	25	81.8(4)	0.02(6)	10.0(2)	0.11(7)	0.63(9)	0.02(3)	0.01(2)	0.37(6)	3.4(2)	3.21(10)	99.57
GBR-5	15	25	76.9(4)	0.06(8)	12.6(3)	0.03(4)	0.79(12)	0.05(6)	0.04(3)	0.49(5)	4.3(2)	3.96(13)	99.22
GBR-2	20	25	74.6(4)	0.10(11)	13.7(3)	0.01(2)	0.82(8)	0.08(4)	0.05(3)	0.58(7)	4.7(2)	4.43(15)	99.07
GBR-6	25	25	73.0(3)	0.26(16)	14.6(3)	0.02(4)	0.87(10)	0.02(3)	0.05(3)	0.60(6)	4.98(16)	4.64(16)	99.04
GBR-11	30	25	71.0(6)	0.17(14)	15.5(3)	0.04(5)	1.10(13)	0.04(4)	0.05(5)	0.59(5)	5.32(15)	5.27(17)	99.08
GBR-10	35	26	70.5(4)	0.05(8)	15.8(3)	0.08(6)	1.10(12)	0.07(4)	0.10(3)	0.63(6)	5.35(16)	5.33(17)	99.01
Reversal and Variable Duration Experiments													
GBR-14	15	20	77.1(3)	0.05(7)	12.28(10)	0.02(3)	0.67(9)	0.09(3)	0.07(3)	0.51(4)	4.01(14)	4.11(13)	98.91
GBR-15	15	20	78.7(4)	0.0(0)	11.30(18)	0.01(2)	0.61(8)	0.06(4)	0.04(2)	0.49(5)	3.90(15)	3.84(13)	98.95
GBR-17	15	20	76.4(4)	0.12(13)	12.6(4)	0.01(3)	0.76(10)	0.10(3)	0.05(2)	0.53(4)	4.16(17)	4.25(14)	98.98
GBR-12	15	25	76.4(5)	0.04(7)	12.88(19)	0.05(3)	0.78(7)	0.09(4)	0.07(3)	0.55(4)	4.22(12)	4.29(9)	99.37
GBR-18	15	25	77.1(3)	0.11(8)	12.3(2)	0.03(3)	0.78(8)	0.07(5)	0.08(2)	0.48(4)	4.3(3)	4.16(11)	99.41
GBR-19	15	25	77.0(4)	0.13(9)	12.4(3)	0.06(4)	0.75(9)	0.06(4)	0.06(2)	0.49(4)	4.4(2)	4.22(13)	99.57

Notes: Analyses are reported in wt%. Units in parentheses represent 1 σ uncertainties of least units cited on the basis of the distribution of replicate analyses. Thus, 77.2(3) should be read as 77.2±0.3.

¹Analysis of glass produced experimentally at 10 kbar, 1500°C.

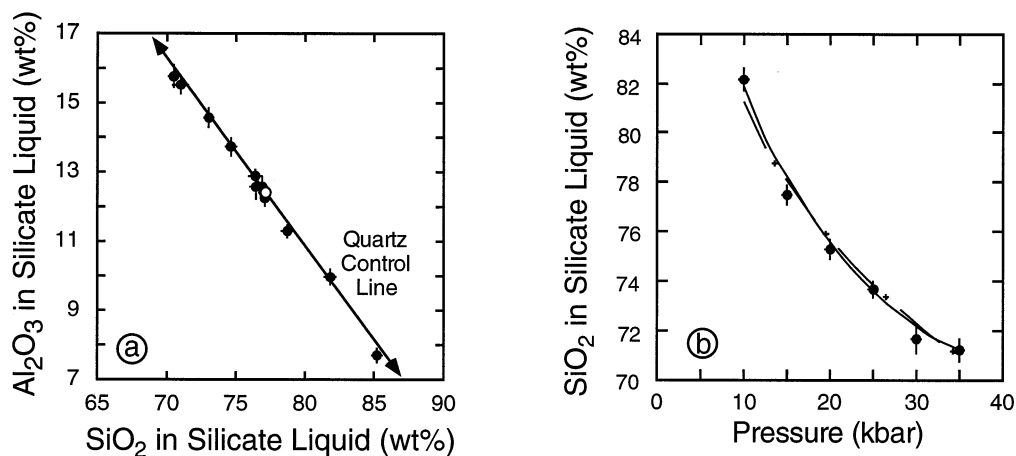


Fig. 1. (a) Plot of wt% SiO₂ vs. wt% Al₂O₃ comparing the compositions of quartz- and cristobalite-saturated silicate liquids produced experimentally at pressures of 1 bar to 35 kbar and temperatures of 1350°C and 1450°C (filled circles) with a quartz control line passing through the bulk composition of Glass Buttes rhyolite (open circle). (b) Plot of wt% SiO₂ vs. pressure illustrating the change in SiO₂ content of quartz-saturated rhyolitic liquids (filled circles) as a function of pressure at 1350°C. Solid curve represents silicate liquid SiO₂ contents calculated using our best fit linear model of the partial molar volume of SiO₂ in these liquids. It was determined by first calculating $\Delta\mu_{\text{SiO}_2}$ at each experimental pressure using Eqn. 5. The calculated $\Delta\mu_{\text{SiO}_2}$ values were then subtracted from $\mu_{\text{SiO}_2}^{\beta\text{-Qtz}}(P,T)$ to determine $\mu_{\text{SiO}_2}^{\text{liq}}(1\text{ bar},T,X)$ corresponding to each experimental pressure. The appropriate SiO₂ contents were determined by using the mixing model of Ghiorso and Sack (1995) to calculate $\mu_{\text{SiO}_2}^{\text{liq}}(1\text{ bar},T,X)$ values for rhyolitic liquids falling along a quartz control line passing through the bulk composition of Glass Buttes rhyolite, then comparing these values with the $\mu_{\text{SiO}_2}^{\text{liq}}(1\text{ bar},T,X)$ values calculated by subtracting $\Delta\mu_{\text{SiO}_2}$ from $\mu_{\text{SiO}_2}^{\beta\text{-Qtz}}(P,T)$. Dashed curve with crosses represents liquid SiO₂ contents predicted as described above using a 4th order Birch-Murnaghan equation of state forced through the data of Lange and Carmichael (1987) and of Kress and Carmichael (1991) at 1 bar and fit to our data at 10 to 35 kbar. The SiO₂ contents of experimentally produced liquids have been normalized to 100% for comparison with predicted SiO₂ contents. For clarity, only the results from 24 h synthesis experiments are shown. Compositional error bars in both figures are 1 σ values from Table 2. Pressure error bars are ± 0.5 kbar.

4. RESULTS AND DISCUSSION

4.1. Compositions of Experimentally Produced Silicate Liquids

The starting mixtures, conditions, and experimental products for each of the experiments are listed in Table 1. The compositions of all experimentally produced liquids are listed in Table 2. The experiments produced homogeneous liquids saturated with quartz at pressures of 10 to 35 kbar and temperatures of 1350 and 1450°C and with cristobalite at 1 bar and 1350°C. The liquid compositions lie along a quartz control line passing through the composition of the Glass Buttes rhyolite starting material (Fig. 1a). The concentrations of SiO₂ in the β -quartz-saturated liquids produced at 1350°C decrease systematically from 81.8 ± 0.4 wt% at 10 kbar to 70.5 ± 0.4 wt% at 35 kbar (Fig. 1b). The rate of decrease of the SiO₂ concentration in the liquids decreases with increasing pressure. The 1 bar experimental liquid saturated with metastable cristobalite contains 85.2 ± 0.4 wt% SiO₂.

The approach to equilibrium represented by our experimentally produced liquids was evaluated by performing a series of experiments with durations ranging from 3 to 72 h at 15 kbar and 1350°C and by performing a temperature reversal at 15 kbar (Tables 1 and 2; Fig. 2). The concentrations of SiO₂ in the liquids produced in the short duration experiments (3 and 8 h) are systematically lower (76.4 ± 0.4 and 76.4 ± 0.5 wt%, respectively) than in the liquids produced by the longer duration experiments (76.9 ± 0.4 wt% after 24 h; 77.1 ± 0.3 wt% after

48 h; 77.0 ± 0.4 wt% after 72 h) but all of the SiO₂ contents overlap at the 2 σ uncertainty level, indicating that a constant liquid composition is attained in 24 h or less at these conditions.

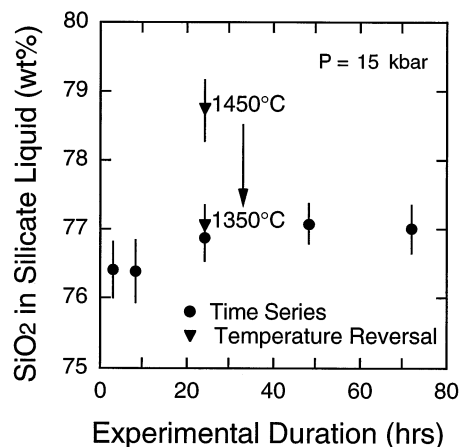


Fig. 2. Plot of wt% SiO₂ vs. experimental duration showing the SiO₂ content of quartz-saturated rhyolitic liquids produced in variable duration synthesis experiments conducted at 15 kbar and 1350°C (filled circles). Also shown are the results of a synthesis experiment conducted at 15 kbar and 1450°C and of a temperature reversal experiment (filled downward-pointing triangles) run first at 15 kbar and 1450°C for 24 h, after which the temperature was dropped to 1350°C and the experiment continued isothermally for an additional 24 h. Error bars are 1 σ values from Table 2.

TABLE 3. Thermodynamic parameters for each experimental liquid composition used to calculate the partial molar volume of SiO₂.

Experiment	P (kbar)	SiO ₂ (wt%)	$\mu_{\text{SiO}_2}^{\beta\text{Qtz}}(P, T)^1$ (kJ/mol)	$\mu_{\text{SiO}_2}^{\text{liq}}(1\text{bar}, T, X)^2$ (kJ/mol)	$\Delta\mu_{\text{SiO}_2}^3$ (kJ/mol)
GBR-3	10	81.8(4)	-1041.9±1.9	-1067.7±1.6	25.7±1.2
GBR-5	15	76.9(4)	-1030.2±1.9	-1068.9±1.6	38.7±1.2
GBR-2	20	74.6(4)	-1018.6±1.9	-1069.6±1.6	51.0±1.1
GBR-6	25	73.0(3)	-1007.1±1.9	-1070.1±1.6	63.0±1.2
GBR-11	30	71.0(6)	-995.6±1.9	-1070.9±1.6	75.3±1.2
GBR-10	35	70.5(4)	-984.2±1.8	-1071.1±1.6	86.9±1.1

Notes: 1 σ uncertainties calculated using Monte Carlo methods with compositional uncertainties taken from the standard deviation of the distribution of electron microprobe analyses, and pressure and temperature uncertainties of ± 0.5 kbar and ± 10 °C, respectively.

¹Calculated using thermochemical and volume data compiled by Berman (1988).

²Calculated using the mixing model of Ghiorso and Sack (1995).

³Uncertainty in $\Delta\mu_{\text{SiO}_2}$ allows for uncertainty of ± 10 °C in temperature, but assumes that quartz and liquid are at the same temperature; hence the uncertainty in $\Delta\mu_{\text{SiO}_2}$ is smaller than the uncertainty in either $\mu_{\text{SiO}_2}^{\beta\text{Qtz}}(P, T)$ or $\mu_{\text{SiO}_2}^{\text{liq}}(1\text{bar}, T, X)$ taken individually.

The temperature reversal was performed by holding the charge at 15 kbar and 1450°C for 24 h to produce a liquid containing 78.7 ± 0.4 wt% SiO₂ (based on the results of GBR-15). The temperature was then decreased at a rate of 100°C/min to 1350°C, and held at that temperature for an additional 24 h. The final liquid composition produced in this experiment (77.1 ± 0.3 wt% SiO₂) is within analytical uncertainty of the liquid produced in the direct synthesis experiment, confirming that 24 h is adequate to achieve a close approach to equilibrium at these conditions.

4.2. The Partial Molar Volume of SiO₂ in Silicate Liquids at Pressures up to 35 kbar

Table 3 lists values of the chemical potential of SiO₂ calculated for each of the experimentally produced liquids reported in Table 2. Thermochemical and volume data from Berman (1988) were used to calculate $\mu_{\text{SiO}_2}^{\beta\text{Qtz}}(P, T)$, and the mixing model of Ghiorso and Sack (1995) was used to calculate $\mu_{\text{SiO}_2}^{\text{liq}}(1\text{bar}, T, X)$. At the experimental conditions, μ_{SiO_2} in the liquid (i.e., $\mu_{\text{SiO}_2}^{\beta\text{Qtz}}(P, T)$ in Eqns. 2–4) increases monotonically with increasing pressure, from -1041.9 ± 1.9 kJ/mol at 10 kbar and 1350°C, to -984.2 ± 1.8 kJ/mol at 35 kbar and 1350°C (Fig. 3). At 1 bar and 1350°C, μ_{SiO_2} in the liquid (i.e., $\mu_{\text{SiO}_2}^{\text{liq}}(1\text{bar}, T, X)$ in Eqns. 3 and 4) calculated using the mixing model of Ghiorso and Sack (1995) decreases slightly with decreasing concentration of SiO₂ in the liquid, from -1067.6 ± 1.6 kJ/mol for the liquid composition produced at 10 kbar containing 81.8 \pm 0.4 wt% SiO₂ to -1071.1 ± 1.6 kJ/mol for the liquid composition produced at 35 kbar containing 70.5 \pm 0.4 wt% SiO₂ (Fig. 3). The Gibbs free energy of tridymite, the stable SiO₂ polymorph at 1 bar and 1350°C, from the compilation of Berman (1988) is -1066.4 kJ/mol, consistent with all of the

experimentally produced liquids being tridymite-undersaturated at these conditions. The difference between the chemical potential of SiO₂ in the liquid at the experimental conditions and at 1 bar ($\Delta\mu_{\text{SiO}_2}$; see Eqn. 3) increases with increasing pressure (Fig. 4a).

The $\Delta\mu_{\text{SiO}_2}$ values were fit to a second-order polynomial in P:

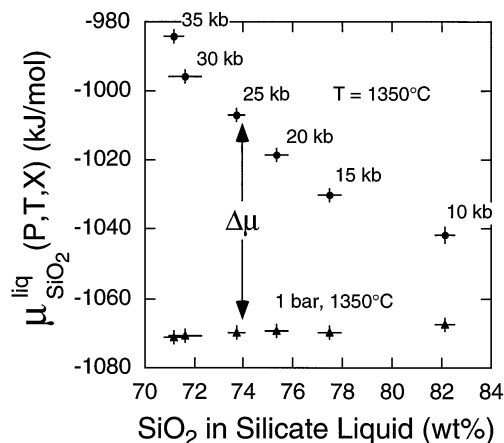


Fig. 3. Plot of the chemical potential of SiO₂ in silicate liquids ($\mu_{\text{SiO}_2}^{\text{liq}}(P, T, X)$) vs. wt% SiO₂. The $\mu_{\text{SiO}_2}^{\text{liq}}(P, T, X)$ values were calculated for each experimentally produced liquid at (1) the high pressure experimental conditions at which the liquid is quartz-saturated, based on the thermochemical and volume data for β -quartz of Berman (1988) (filled circles) and (2) at 1 bar and 1350°C, calculated using the mixing model of Ghiorso and Sack (1995) (filled triangles). For clarity, only the results from 24 h synthesis experiments are shown. Compositional error bars are 1 σ values from Table 2. Chemical potential uncertainties are 1 σ values from Table 3.

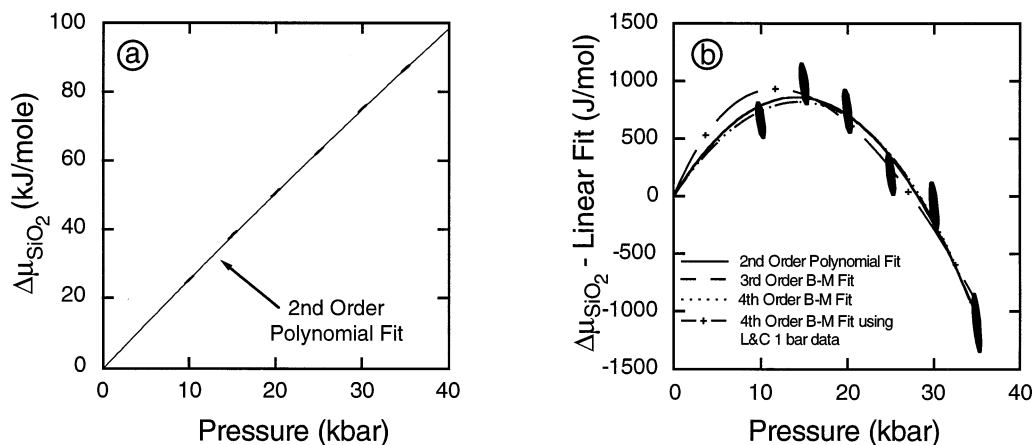


Fig. 4. (a) Plot of the difference between the chemical potential of SiO₂ in experimentally produced quartz-saturated silicate liquids at experimental conditions and at 1 bar and 1350°C ($\Delta\mu_{\text{SiO}_2}$ from Table 3 and Fig. 3) vs. pressure comparing experimental results with a second order polynomial fit to the data (Eqn. 5). Error ellipses are 1σ . Uncertainties attributable to liquid composition and experimental temperature ($\pm 10^\circ\text{C}$) were calculated using Monte Carlo methods. Uncertainty associated with experimental pressures were determined by calculating the range of chemical potential of SiO₂ associated with a pressure range of ± 0.5 kbar. (b) Plot illustrating the deviation from linearity of the difference between the chemical potential of SiO₂ in experimentally produced quartz-saturated silicate liquids at experimental conditions and at 1 bar, 1350°C ($\Delta\mu_{\text{SiO}_2}$) as a function of pressure (i.e., the deviation from a constant partial molar volume of SiO₂). The solid curve represents a second-order polynomial fit to the data (Eqn. 5), the dashed curve represents the fit to a third-order Birch-Murnaghan equation of state, the dotted curve represents the fit to a fourth-order Birch-Murnaghan equation of state, and the dashed curve with crosses represents the fit to a fourth-order Birch-Murnaghan equation of state assuming the 1 bar values of $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ from Lange and Carmichael (1987) and of $(\partial\bar{V}_{\text{SiO}_2}^{\text{liq}}/\partial P)_T$ from Kress and Carmichael (1991). Error ellipses are as in Fig. 4a.

$$\Delta\mu_{\text{SiO}_2} = 2.635 \pm 0.009(P - 1) - \frac{1}{2} 8.69 \cdot 10^{-6} \pm 6.1 \cdot 10^{-7}(P - 1)^2 \text{ J} \quad (5)$$

where P is in bars. The r^2 value of the fit is 0.999986 and the χ^2 value is 4.01 (Fig. 4; Table 4). The χ^2 value is not improved significantly by fitting to a third-order polynomial ($\chi^2 = 3.79$). The derivative of Eqn. 5 with respect to pressure gives the partial molar volume of SiO₂ in the liquids as a function of pressure:

$$\frac{\partial\Delta\mu_{\text{SiO}_2}}{\partial P} = \bar{V}_{\text{SiO}_2}^{\text{liq}} = 2.635 \pm 0.009 - 8.69 \cdot 10^{-6} \pm 6.1 \cdot 10^{-7}(P - 1) \text{ J/bar} \quad (6)$$

based on Eqn. 4. The 1 bar partial molar volume for SiO₂ ($\bar{V}_{\text{SiO}_2}^{\text{liq},0}$) determined in this way, 2.635 ± 0.009 J/bar, similar to but lower than the $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ value of 2.690 ± 0.006 J/bar given by Lange and Carmichael (1987) and the value of 2.675 J/bar given by Bottinga et al. (1982). The isothermal pressure dependence of the partial molar volume of SiO₂ ($(\partial\bar{V}_{\text{SiO}_2}^{\text{liq}}/\partial P)_T$) given by Eqn. 6, $-8.69 \times 10^{-6} \pm 6.1 \times 10^{-7}$ J/bar², is approximately one-half of the 1 bar value given by Kress and Carmichael (1991) ($-1.96 \times 10^{-5} \pm 0.2 \times 10^{-6}$ J/bar²) (Fig. 5a). The “bulk modulus” of the SiO₂ component in the liquid (which we define as $=K_T(P) = -\bar{V}_{\text{SiO}_2}^{\text{liq}}(dP/d\bar{V}_{\text{SiO}_2}^{\text{liq}})_T$) calculated using the extrapolation of our high pressure data to 1 bar is 303 ± 21 kbar, while a value of 138 ± 1 kbar is obtained using the 1 bar data of Lange and Carmichael (1987) and Kress and Carmichael (1991) (Table 4).

The uncertainties reported in Table 3 are based only on electron microprobe measurement statistics and experimental temperature and pressure uncertainties (assumed to be Gaussian). There is, however, the potential for an additional systematic error due to the use of the mixing model of Ghiorso and Sack (1995) to calculate $\mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar}, T, X)$ for each of the experimentally produced liquids. There are no data that independently constrain the values of $\mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar}, T, X)$ for our experimental liquids, so it is difficult to assign precise values to the systematic errors that may be associated with the mixing model. Comparison to other experimental datasets (e.g., feldspathoid-feldspar-liquid equilibria) suggests that the chemical potential for SiO₂ given by the mixing model of Ghiorso and Sack (1995) is reasonable for rhyolitic liquids (Sack and Ghiorso, 1998). A comparison of the chemical potential of SiO₂ in our 1 bar experimental liquid calculated using the mixing model (-1066.8 kJ/mol) with the Gibbs free energy of cristobalite at these conditions (-1066.4 kJ/mol) from the compilation of Berman (1988) indicates a relatively small but nonnegligible discrepancy of 440 ± 60 J/mol. However, the 1 bar cristobalite-saturated liquid has significantly higher SiO₂ (85.2 ± 0.4 wt%) than the high pressure quartz-saturated liquids used to determine the partial molar volume of SiO₂ (70.5 ± 0.4 to 81.8 ± 0.4 wt%); since the compositional range of the high pressure liquids overlaps with the data used to calibrate the mixing model of Ghiorso and Sack (1995) (whereas the 1 bar cristobalite-saturated liquid falls outside of this range), this value of ~ 400 – 500 J/mol probably overestimates the systematic uncertainties associated with the calculated values of $\mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar}, T, X)$. As described in the next paragraph, for

TABLE 4. One bar partial molar volumes and elastic parameters for SiO₂ component in silicate liquid derived by assuming different functional forms for the relationship between partial molar volume and pressure.

Functional form	$\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ (J/bar)	K_T^0 (bar)	K_T'	K_T'' (bar ⁻¹)	χ^2
Linear ¹	2.635±0.009	303±21×10 ³	—	—	4.01
3rd Order Birch-Murnaghan	2.625 ^{+0.02} _{-0.013}	354 ⁺⁶⁷ ₋₁₂₈ ×10 ³	-2.0 ^{+6.6} _{-1.2}	—	3.82
4th Order Birch-Murnaghan	2.626 ^{+0.02} _{-0.05}	326 ⁺⁶⁹ ₋₂₄₃ ×10 ³	1.1 ^{+24.6} _{-2.1}	-2.1 ^{+4.0} _{-0.92} ×10 ⁴	3.81
4th Order Birch-Murnaghan ²	2.690±0.006	138±1×10 ³	0.6 ^{+6.9} _{-3.4}	2.0 ⁺¹³ _{-1.7} ×10 ³	8.09

Notes: χ^2 values reflect goodness of fit of $\Delta\mu_{\text{SiO}_2}$ -P pairs to assumed functional forms for the integral of volume with respect to pressure (i.e., equation (3)). Uncertainties for the linear fit and for $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ and K_T^0 from the 4th order Birch-Murnaghan equation of state in which the 1 bar data of Lange and Carmichael (1987) and of Kress and Carmichael (1991) were used were calculated from 1 σ uncertainties associated with $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ and $(\partial\bar{V}_{\text{SiO}_2}^{\text{liq}}/\partial P)_T$. All other uncertainties were calculated by varying the parameter and best-fitting the remaining parameters until a $\Delta\chi^2 = 1$ was achieved.

¹ $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ and $(\partial\bar{V}_{\text{SiO}_2}^{\text{liq}}/\partial P)_T$ from equation 6 were used to calculate K_T^0 . The relationship between $\bar{V}_{\text{SiO}_2}^{\text{liq}}$ and pressure is $\bar{V}_{\text{SiO}_2}^{\text{liq}} = \bar{V}_{\text{SiO}_2}^{\text{liq},0} - \bar{V}_{\text{SiO}_2}^{\text{liq},0} (K_T^0)^{-1} (P-1)$

² $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ and K_T^0 values were forced to the 1 bar values of Lange and Carmichael (1987) and Kress and Carmichael (1991), then K_T' and K_T'' were derived using the minimization routine described in the text.

the purposes of the current exercise we prefer to constrain the maximum systematic error on $\mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar}, T, X)$ by using the goodness-of-fit of our data to volume functions, which in turn allows an estimate of the uncertainty in the fitted volume parameters due to systematic error.

Because our data were fit to the integral of volume from 1 bar to P (i.e., Eqn 3), the fitted curve in Fig. 4a must pass through zero at 1 bar (i.e., $\Delta\mu_{\text{SiO}_2}$ must equal zero at 1 bar). Furthermore, linear, quadratic, or Birch-Murnaghan fits to volume yield smooth functions in $\Delta\mu_{\text{SiO}_2}$ -P space (e.g., Fig. 4a). If all the $\Delta\mu_{\text{SiO}_2}$ values were systematically offset from those reported in Table 3, it would become increasingly difficult to fit a smooth curve that passes through zero at 1 bar to all of the data. It is possible that the systematic errors associated with the mixing model of Ghiorso and Sack (1995) are large and yet vary with composition in such a way as to yield a smooth curve in Fig. 4a, but this would be fortuitous. The requirement that our data fit a smooth volume function can, therefore, be used to constrain the magnitude of simple forms for the systematic error. We tested the strength of this constraint with a series of synthetic fits in which a constant offset in $\Delta\mu_{\text{SiO}_2}$ was added to each of our six P- $\Delta\mu_{\text{SiO}_2}$ pairs, and they were refit to second- and third-order polynomials (e.g., Eqn. 5). The χ^2 value of the second-order polynomial fit in Eqn. 5 is 4.01. This goodness-of-fit parameter increases with the square of the $\Delta\mu_{\text{SiO}_2}$ offset, for either positive or negative offsets; i.e., there is a well-defined minimum at an offset of zero (Fig. 6). An offset of ± 400 J/mol increases the χ^2 value by one, which is equivalent to a one standard error confidence interval. The corresponding 1 σ uncertainty in $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ is ± 0.04 J/bar and in $(\partial\bar{V}_{\text{SiO}_2}^{\text{liq}}/\partial P)_T$ is $\pm 2 \times 10^{-6}$ J/bar² (i.e., about 25% relative in $(\partial\bar{V}_{\text{SiO}_2}^{\text{liq}}/\partial P)_T$).

We also tested a series of synthetic fits where it was assumed that the systematic error due to the mixing model of Ghiorso and Sack (1995) is zero for a pure SiO₂ liquid and increases as a linear function (100 – wt% SiO₂). Again, χ^2 increases quadratically with the slope of the offset and has a well-defined minimum at a slope of zero (i.e., no systematic error). The $\Delta\chi^2 = 1$ half-width for these fits is an uncertainty in slope of ± 15 J/wt% SiO₂, or ± 300 J/mol for the 35 kbar datum, resulting in 1 σ uncertainties of ± 0.03 J/bar in $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ and $\pm 1 \times 10^{-6}$ J/bar² in $(\partial\bar{V}_{\text{SiO}_2}^{\text{liq}}/\partial P)_T$ for this assumed form of the error. Note that the uncertainties indicated by either assumed form for the systematic error are in the range indicated by the results from our 1 bar experiment.

The uncertainties associated with either assumed form of the systematic error are considerably larger than the uncertainties due to random error alone (± 0.009 J/bar in $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ and $\pm 6 \times 10^{-7}$ J/bar² in $(\partial\bar{V}_{\text{SiO}_2}^{\text{liq}}/\partial P)_T$). However, these uncertainties are small enough that our data overlap the Lange and Carmichael (1987) value for $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ only for uncertainties close to 2 σ when both random and systematic errors are considered. The $(\partial\bar{V}_{\text{SiO}_2}^{\text{liq}}/\partial P)_T$ value at 10 to 35 kbar indicated by our results is significantly lower than the 1 bar value of Kress and Carmichael (1991) even when both systematic and random errors are considered. Hence, in the absence of experiments that directly constrain the quality of the $\mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar}, T, X)$ values obtained for our experimental liquids from the mixing model, the current data are most consistent with systematic errors that are less than ≈ 0.5 kJ/mol, making it improbable that the differences between our fitted volume function and the 1 bar results of Lange and Carmichael (1987) and of Kress and Carmichael (1991) are due solely to systematic errors in the

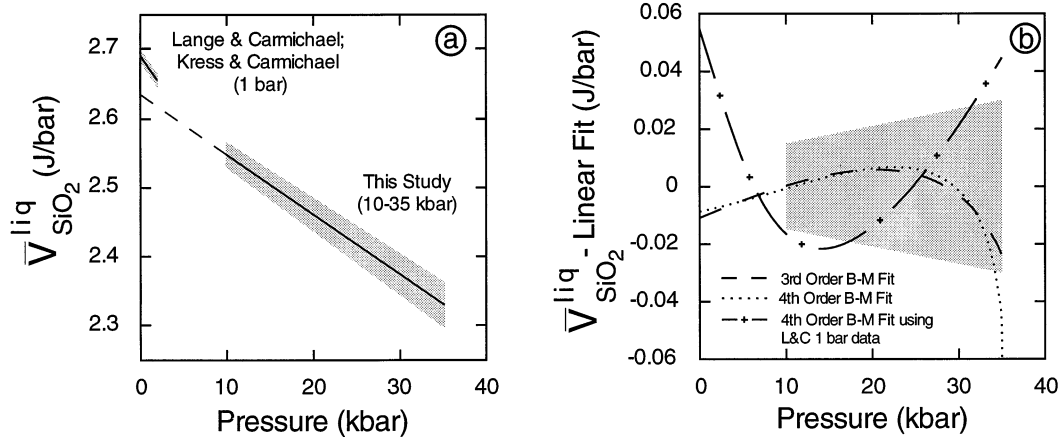


Fig. 5. (a) Plot of the partial molar volume of SiO_2 in silicate liquids as a function of pressure at 1350°C from the 1 bar determinations of Lange and Carmichael (1987) and of Kress and Carmichael (1991) and the high pressure determination presented in this study (10 to 35 kbar). Dashed line represents an extrapolation of Eqn. 6 to 1 bar. The 1 bar data have been extrapolated to higher pressures for clarity. Shaded regions represent 1σ uncertainties calculated on the basis of the regression parameter uncertainties. (b) Plot illustrating the deviation from linear pressure dependence of the partial molar volume of SiO_2 in silicate liquids (i.e., deviation from the partial molar volumes predicted by Eqn. 6) calculated by assuming different functional forms for the relationship between $\Delta\mu_{\text{SiO}_2}$ and pressure. The dashed curve represents a fit of our data to a third-order Birch-Murnaghan equation of state, and the dotted curve represents a fit of our data to a fourth-order Birch-Murnaghan equation of state. The dashed curve with crosses represents a fit of our data to a fourth-order Birch-Murnaghan equation of state in which the $\bar{V}_{\text{SiO}_2}^{\text{liq},0}$ and K_T^0 calculated from the 1 bar data of Lange and Carmichael (1987) and of Kress and Carmichael (1991) were assumed (2.690 ± 0.006 J/bar and 138 ± 1 kbar, respectively). Shaded region is the same as in (a).

mixing model of Ghiorso and Sack (1995) unless the variation of such errors with composition fortuitously conspires to force our data to a smooth curve that passes through zero at 1 bar.

Given these results, the differences between our extrapolated 1 bar partial molar volume for SiO_2 and its isothermal pressure dependence and the values given by Lange and Carmichael (1987) and by Kress and Carmichael (1991) plausibly reflect

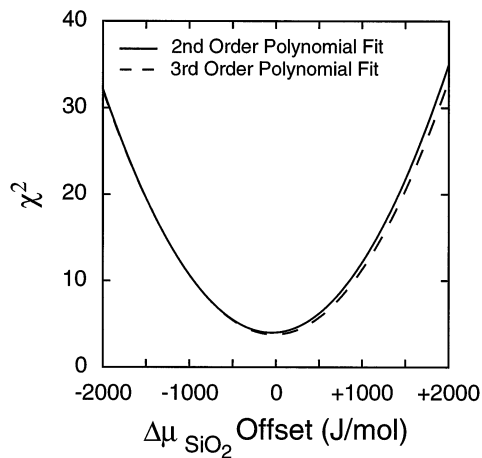


Fig. 6. Plot of χ^2 vs. $\Delta\mu_{\text{SiO}_2}$ offset showing the results from a series of synthetic fits in which a constant offset in $\Delta\mu_{\text{SiO}_2}$ was added to each of our six (P , $\Delta\mu_{\text{SiO}_2}$) pairs, which were then refit to second- and third-order polynomials. This illustrates the effect of one possible form of systematic error associated with using the mixing model of Ghiorso and Sack (1995) to calculate $\mu_{\text{SiO}_2}^{\text{liq}}(1 \text{ bar}, T, X)$ for our experimental liquids. An increase in χ^2 of 1 is equivalent to a one standard error confidence interval.

the fact that their values are based on 1 bar data whereas our data are all from pressures of 10 kbar or higher where the liquid is less compressible. The isothermal pressure derivative of the partial molar volume of SiO_2 may thus decrease with increasing pressure from the 1 bar value of Kress and Carmichael (1991) to the approximately constant value we have determined; if this is the resolution of the apparent discrepancies between these determinations, the approximately constant high pressure value would be achieved at ~ 7 kbar; i.e., the pressure at which the partial molar volumes for SiO_2 from the different approaches converge (Fig. 5a). This would imply that the compressibility of the SiO_2 component decreases rapidly between 1 bar and 10 kbar. Such a change in compressibility is similar to that proposed for albitic liquid by Navrotsky et al. (1982) in order to reconcile 1 bar thermochemical and volume data for $\text{NaAlSi}_3\text{O}_8$ with the Clapeyron slope of the fusion curve at 10 to 30 kbar. Further experiments in the pressure range 1 bar to 10 kbar are needed to reconcile fully the differences between the high- and low-pressure volume data for the SiO_2 component in silicate liquids. It is possible, for example, that these differences reflect, in part, failure of the assumption that the partial molar volume of SiO_2 is independent of composition over the range of liquid compositions produced in this study, or some other limitation in the assumptions underlying our data analysis.

In addition to simple polynomial forms for the pressure dependence of $\Delta\mu_{\text{SiO}_2}$, our data were fit to P - $\bar{V}_{\text{SiO}_2}^{\text{liq}}$ relationships corresponding to third-order and fourth-order Birch-Murnaghan equations of state for a homogeneous phase (Birch, 1978; Meade and Jeanloz, 1987) (Fig. 4b). In contrast to the linear least-squares fitting method recommended by Birch

(1978), which requires data in the form of pressure-volume or pressure-strain pairs, we used a nonlinear multidimensional downhill minimization routine (Press et al., 1992) to fit the $P\text{-}\Delta\mu_{\text{SiO}_2}$ pairs to Eqn. 3 (the integral of VdP was obtained from the Birch-Murnaghan expression for $P(V)$ using integration-by-parts). The best-fit $\bar{V}_{\text{SiO}_2}^{\text{liq},o}$ for a third-order Birch-Murnaghan equation of state is $2.625^{+0.02}_{-0.013}$ J/bar and the best-fit zero-pressure “bulk modulus” for the liquid SiO₂ component (K_T^0) is 354^{+67}_{-128} kbar (Table 4). These values are not significantly different from the $\bar{V}_{\text{SiO}_2}^{\text{liq},o}$ (2.635 ± 0.009 J/bar) and K_T^0 (303 ± 21 kbar) of the linear fit to volume in Eqn. 6 despite the difference in the functional forms of the fits (Fig. 5b). The third-order fit gives a negative pressure derivative for $K_T(P)$ ($K_T' = -2^{+6.6}_{-1.2}$), while the fourth-order fit gives a 1 bar K_T' value of $1.1^{+24.6}_{-2.1}$ and second pressure derivative for $K_T(P)$ that is negative ($K_T'' = -2.1^{+4.0}_{-0.92} \times 10^{-4}$ bar⁻¹) such that $K_T(P)$ decreases with increasing P over the experimental range of 10 to 35 kbar for both the third- and fourth-order fits. The χ^2 values of the three-parameter (3.82) and four-parameter (3.81) fits, however, are not significantly better than the simple two-parameter linear fit (4.01) of Eqn. 6 (Table 4). Moreover, use of the 3rd or 4th order Birch-Murnaghan equations of state produces nearly identical fits to the $\Delta\mu_{\text{SiO}_2}$ vs. P data that are, in turn, essentially identical to the polynomial $\Delta\mu_{\text{SiO}_2}$ vs. P functions (Fig. 4b). The same can also be said of the P vs. V fits (Fig. 5b). Finally, we fit our data to a fourth-order Birch-Murnaghan equation of state assuming the $\bar{V}_{\text{SiO}_2}^{\text{liq},o}$ and K_T^0 calculated from the 1 bar data of Lange and Carmichael (1987) and of Kress and Carmichael (1991) (2.690 ± 0.006 J/bar and 138 ± 1 kbar, respectively). This yields values of $-0.6^{+6.9}_{-8.4}$ and $2.0^{+1.3}_{-1.7} \times 10^{-3}$ bar⁻¹ for the first and second pressure derivatives of $K_T(P)$, respectively (Table 4; Figs. 4b and 5b) with an unsatisfactory χ^2 value of 8.09. This fit extrapolates poorly to high pressure because of the large positive K_T'' , and misses our 10 kbar datum for $\Delta\mu_{\text{SiO}_2}$ by $>2\sigma$ (Fig. 4b). Therefore, if the 1-bar and high-pressure data are consistent, the body of available results indicates that neither simple low-order polynomials in P nor low-order functions derived from finite-strain theory appear to be entirely appropriate for fitting partial molar volume data for silicate liquid components. Additional data and more theoretical studies of the volume properties of silicate liquids may be required to find a more suitable equation of state formalism.

Note that the negative K_T' given by the 3rd-order Birch-Murnaghan fit is a well-established feature of both SiO₂ and pyrex glasses at low pressure and temperature (Bridgman, 1925, 1939; McSkimin, 1957; Bogardus, 1965; Peselnick et al., 1967; Kondo et al., 1981; Meade and Jeanloz, 1987). Although it may be coincidental (in particular, there should not necessarily be any correspondence between of the properties of glass at room temperature and those of liquids at high temperatures), the values of K_T^0 for the SiO₂ glass (365 to 371 kbar from the studies cited above) and the SiO₂ component in the liquid (303 to 354 kbar depending on functional form) are also similar. We do not wish to place too much weight on the Birch-Murnaghan fits in preference to the simple polynomial fit, but this similarity between the pressure dependence of the partial molar volume of SiO₂ based on the fit to our data and the seemingly anomalous bulk properties of SiO₂-rich glasses (i.e., the increase in

compressibility with increasing pressure) is intriguing and should be evaluated in future studies.

5. CONCLUSIONS

The partial molar volume of an oxide component in silicate liquids and its pressure derivative can be determined at high pressures and temperatures from an experimental determination of the isothermal pressure-dependence of the solubility in the liquids of a crystalline phase having the composition of the oxide, given (1) the assumption that the partial molar volume of the oxide component is independent of composition over the range of liquid compositions, (2) knowledge of the thermochemistry and equation of state of the crystalline phase, and (3) knowledge of the 1 bar activity-composition relationship of the liquid component. This approach can, in principle, also be used to determine the partial molar volume and compressibility of silicate mineral components such as forsterite in the liquid. Because this approach allows the determination of partial molar volumes of liquid components *at elevated pressure*, it has the potential to detect pressure-sensitive structural changes associated with particular components in silicate liquids through their influence on the partial molar volumes of these components.

We have applied this approach to SiO₂ by measuring the pressure dependence of quartz solubility in a rhyolitic liquid at 10 to 35 kbar and 1350°C. Extrapolation of our results to 1 bar results in a partial molar volume for SiO₂ that is similar to, but lower than, the values determined by Lange and Carmichael (1987) and by Bottinga et al. (1982). The isothermal pressure derivative of the partial molar volume of SiO₂ at 10 to 35 kbar given by our experiments is significantly lower than the 1 bar determination of Kress and Carmichael (1991). The low- and high-pressure data can be reconciled if the pressure derivative of the partial molar volume of SiO₂ decreases rapidly between 1 bar and 10 kbar, then remains approximately constant to at least 35 kbar. Although these differences will have to be explored in future work, this new approach has promise to provide accurate and precise information on the partial molar volumes of oxide or mineral components in silicate liquids at high pressures.

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