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Magma density at high pressure Part 1: The effect of composition on the elastic properties of silicate liquids

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Abstract—The effect of composition on the 1 atmosphere isothermal bulk modulus, K^0, of silicate liquids has been evaluated from a thermodynamic analysis of the fusion curves for β–quartz, forsterite, and fayalite in addition to measurements of ultrasonic velocities in silicate melts. Numerical simulations of the fusion curves in temperature–pressure space are very sensitive to the value of K^0 for the liquid phase. However, K^0 determined for liquid SiO_2, Fe_2SiO_4, and Mg_2SiO_4 depends also on the choice of parameters used in the equation of state and, most importantly, the value chosen for the thermal expansivity of the liquid phase. The wide range of reported values have been critically evaluated, and a set of model thermal expansivities is offered. Bounds have also been placed on the pressure derivative of the bulk modulus, and it is shown that it must be less than about 6, 4.7, and 4 for liquid SiO_2, Fe_2SiO_4, and Mg_2SiO_4, respectively. The K^0 for liquid SiO_2 determined from the fusion curve of β–quartz is in good agreement with that determined by light scattering methods. The K^0 for liquid Fe_2SiO_4 determined from the fusion curve of fayalite is exceptionally well constrained because it is based on a comprehensive set of thermodynamic and elastic parameters that are internally consistent with all experimental data, including the calorimetry work of STEBBINS and CARMICHAEL (1984); K^0 determined from this fusion curve analysis is much higher than that determined by RIVERS and CARMICHAEL (1986) from ultrasonic measurements.

Bulk moduli of the oxide components SiO_2, Al_2O_3, FeO, MgO, CaO, SrO, BaO, Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O in silicate liquids at 1400°C and 1 atmosphere have been estimated from complex melt compositions using the Voigt–Reuss–Hill mixing approximation. For liquid FeO and MgO there are two contradictory sets of data; bulk moduli for these deduced from the fusion curve analysis are over 200 percent higher than those deduced from the ultrasonic measurements of RIVERS and CARMICHAEL (1986) on liquid Fe_2SiO_4, and $MgSiO_3$.

It is shown that there exists an inverse relationship between bulk modulus and specific volume for all liquid oxide components in silicate melts when use is made of K^0 for liquid FeO and MgO derived from the fusion curve analysis. Similar observations have been made on crystalline binary compounds (ANDERSON and NAFE, 1965) for which compression can be described by a simple elastic law, the empirical law of corresponding states (ANDERSON, 1966). It is demonstrated that this elastic law holds also for metals in both the liquid and crystalline states. The implication is that the law of corresponding states can be generalized to substances in the liquid and crystalline states for all binary metal–anion chemical systems containing intermediate compounds (*e.g.,* oxides, tellurides, etc.). However, bulk moduli for liquid MgO and FeO deduced from ultrasonic studies on liquid $MgSiO_3$ and Fe_2SiO_4 violate this law.

Silicate liquids which compress in violation of the law of corresponding states support the hypothesis that there exists an olivine–liquid density crossover at upper mantle pressures. However, for a universal elastic law, the assumptions upon which this hypothesis rests are seriously in error and, indeed, are likely to be fatally flawed.

INTRODUCTION

ONE OF THE physical parameters which will determine the transport fate of magmas at depth is the density contrast between coexisting crystalline and liquid phases. Interest in this problem was stimulated by the hypothesis of STOLPER *et al.* (1981) that silicate melts may become neutrally buoyant or even denser than solid residua at high pressures (4 to 8 GPa). This unorthodox idea was based on an analysis of densities of basalts measured to 1.5 GPa (FUJII and KUSHIRO, 1977a,b), and the compressibilities of basaltic melts and various liquids in alkali oxide-SiO_2 systems deduced from ultrasonic measurements. These data demonstrate that the compressibility of basaltic melts is considerably greater than that for typical crystalline silicates such as olivine. RIGDEN *et al.* (1984) corroborated these findings from shock wave measurements on liquid anorthite$_{36}$diopside$_{64}$ (mol percent), a basalt analogue. The possibility that olivine flotation may occur at high pressures has received attention in a number of theories dealing with partial melt processes in the mantle and the internal structure of the Earth (STOLPER *et al.*, 1981; NISBET and WALKER, 1982; WALKER, 1983; HERZBERG, 1984; OHTANI, 1984; RIGDEN *et al.*, 1984).

Another indirect method for determining the compressibility of silicate melts is by analysis of the fusion curves of minerals. Early attempts (*e.g.,* Carmichael *et al.,* 1977) were reexamined by Herzberg (1983) and Ohtani (1984), and the results supported the suggestion that an olivine–magma density crossover may exist, although Herzberg (1983) suggested it may be in the 10–15 GPa range. A more rigorous thermodynamic approach was provided by Bottinga (1985) who noted that the compressibility of silicate liquids depends on its bulk composition. Compressibility increases with SiO_2 content, a result supported by compressibility measurements in the system SiO_2–$NaAlO_2$–$CaAl_2O_4$ below the glass transition (Seifert *et al.,* 1982), and also by the ultrasonic data of Sato and Manghnani (1985).

The effect of bulk composition on the compressibility/bulk modulus of silicate liquids is crucial to the debate because anhydrous magmas at pressures in the mantle where the density crossover is suggested to occur are not basaltic in composition. Rather, initial melts have a considerable amount of olivine in the norm, and range from komatiite to lherzolite in composition (Herzberg, 1983; Takahashi and Scarfe, 1985; Herzberg *et al.,* 1986; Ohtani *et al.,* 1986). Although the question of an olivine-basaltic magma density crossover is petrologically meaningless, there remains considerable merit to the question if it can be established that variations in bulk composition have no effect on the compressibility of silicate liquids. This was the position adopted by Rigden *et al.* (1984), based on the observation that the bulk modulus of an Fe_2SiO_4 liquid determined by Rivers and Carmichael (1986) from ultrasonic velocities is essentially the same as that for the basalt analogue used in their shock wave experiments. If correct, the existence of an olivine–magma density crossover at high pressures is assured. However, Bottinga (1985) calculated that the bulk modulus of liquid Mg_2SiO_4 is 300% higher than that determined from the ultrasonic data of Rivers and Carmichael (1986) on liquid Fe_2SiO_4. If this is correct, then the hypothesis of a density crossover is unconvincing (see Herzberg, 1987).

In order to resolve the question of an olivine–magma density crossover, the compressibility of silicate liquids has been reevaluated with special attention focused on the effect of bulk composition. The examination involves both a thermodynamic analysis of the fusion curves of β–quartz, forsterite, and fayalite and compressibility information determined by light scattering and ultrasonic methods.

The melting curves have been simulated numerically and are compared to experimental data. From an error analysis of the parameters used in these calculations, it is demonstrated that previous attempts at a fusion curve analysis are seriously flawed because they have assumed values of the thermal expansivity of silicate liquids which are in many cases demonstrably in error. It is shown here that their effect on the calculation of the bulk modulus of silicate liquids is huge. Owing to this difficulty, this work is divided into two parts. In Part 1 the effect of composition on the bulk modulus of silicate liquids is examined with considerable attention focused on an evaluation of the uncertainties arising from partial molar volumes and thermal expansivities of the oxide components in silicate melts. The hypothesis of an olivine-magma density crossover is considered in Part 2 (Herzberg, 1987).

FUSION CURVE ANALYSIS

Thermodynamic considerations

The equations used to derive the isothermal bulk modulus of liquid SiO_2, Fe_2SiO_4, and Mg_2SiO_4 are almost identical to those used by Bottinga (1985), although small differences exist in the overall methodology. In this analysis, the fusion curves were calculated by means of a finite element solution to the Clausius-Clapeyron equation:

$$dT/dP = \Delta V/\Delta S \qquad (1)$$

$$= \frac{V_l(T,P) - V_s(T,P)}{\Delta S^0 + P(\alpha_s V_s(T,P) - \alpha_l V_l(T,P)) + \int_{T_f}^{T} \frac{\Delta C_p dT}{T}}. \qquad (2)$$

For the liquid(l) and solid(s) phases, the molar volume, $V(T, 1)$, at temperature T and 1 atmosphere is:

$$V(T,1) = V^0(1 + \alpha(T - T_r) \qquad (3)$$

where α, the isobaric thermal expansivity, is expressed:

$$\alpha = 1/V^0(\partial V/\partial T)_P \qquad (4)$$

and T_r is the standard reference temperature for V^0. For crystalline materials T_r is 25°C; for liquid Mg_2SiO_4 and Fe_2SiO_4 T_r is the fusion temperature T_f, and for the oxides listed in Table 2 T_r is 1400°C. Molar volumes for liquid Mg_2SiO_4, Fe_2SiO_4, and SiO_2 listed in Table 1 were determined from the partial molar volumes of MgO, FeO, and SiO_2 listed in Table 2, assuming no excess volumes of mixing.

Accurate data are now available on the temperature derivative of the thermal expansivity for forsterite and fayalite (Suzuki *et al.,* 1981, 1983). These data were fitted to the equation:

$$\alpha = \alpha^0 + (T - 25)(d\alpha^0/dT) \qquad (5)$$

where α^0 is valid at 25°C. The temperature derivative of the thermal expansivity of β–quartz is not known, but it is expected to be very small; consequently it was set at zero.

Table 1. Thermodynamic and elastic data

	Mg_2SiO_4	Fe_2SiO_4	SiO_2	Dimension
Crystalline Phases				
V^0	43.63[1,2,3]	46.26[1,6,7,8]	23.80[11]	cm^3/gfw
α^0	2.77[3,4]	2.57[9]	−0.65[11]	$\times 10^{-5}/°C$
$d\alpha^0/dT$	1.03[3,4]	0.97[9]	0.00	$\times 10^{-8}/°C^2$
K^0	127.77[3,4]	137.33[8]	37.10[12]	GPa
dK^0/dT	−0.0227[3,4]	−0.0278[8]	0.00	GPa/°C
dK^0/dP	5.39[5]	5[10]	6.2	—
Liquid Phases				
V^0	53.67	52.43	27.08	cm^3/gfw
α^0	10.84	12.42	1.00	$\times 10^{-5}/°C$
$d\alpha^0/dT$	0	0	0	$\times 10^{-8}/°C^2$
dK^0/dT	0	0	0	GPa/°C
Melting Parameters at 1 atmosphere				
T_f	1890[13]	1205[14]	1469[15]	°C
$(dT/dP)_i$	55(5)[16,17]	68(2)[18,19,20]	400(25)[15]	°C/GPa
ΔS^0 [21]	113.1(13.5)	60.88(6.74)	8.7(.8)	J/(gfw · °C)

1 Fisher and Medaris (1969). 2 Hazen (1976). 3 Suzuki *et al.* (1983). 4 calculated from data in 3 by least squares regression. 5 Kumazawa and Anderson (1969). 6 Hazen (1977). 7 Smyth (1975). 8 Sumino (1979). 9 Suzuki *et al.* (1981). 10 assumed: Chung (1979) reports 5.97 which seems excessive (Sawamoto, personal communication; Anderson and Anderson, 1970; Anderson 1972). 11 metastable extension; Skinner (1966). 12 Levien *et al.* (1980). 13 Bowen and Anderson (1914). 14 Bowen and Schairer (1932). 15 metastable melting point; Jackson (1976). 16 Davis and England (1964). 17 Ohtani and Kumazawa (1981). 18 Lindsley (1967). 19 Akimoto *et al.* (1967). 20 Ohtani (1979). 21 calculated; see text.

V^0, α^0, and K^0 for crystalline phases are at 25°C; V^0 and α^0 are model values for liquid phases at T_f.

Many contradictory values have been reported for the thermal expansivity of silicate liquids, and these will receive considerable attention in this analysis. These are listed in Table 2 and shown in Figure 1. New constraints on the thermal expansivities for MgO and FeO have been obtained, and these are discussed below; it is suggested that the thermal expansivities for the oxide components

Table 2. Molar volumes V^0 (cm^3/gfw) at 1400°C and thermal expansivities ($\times 10^5/°C$) for components in silicate liquids

	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	
BW	26.80	37.96	12.80	11.57	16.50	28.90	46.00	V^0
	1.0	2.6	15.6	23.4	18.2	23.8	15.2	α
NC	27.20	36.26	12.64	12.08	16.16	28.57	45.49	V^0
	−1.5	15.1	21.4	15.8	39.9	24.6	26.3	α
MCRS	27.03	36.63	13.86	11.43	16.32	28.78	45.93	V^0
	−0.7	14.8	31.5	9.5	38.4	23.5	24.9	α
BWR	26.75	—	13.94	12.32	16.59	29.03	46.30	V^0
	0.1	—	33.4	12.2	17.0	25.9	37.3	α
SCM	26.75	37.69	13.67	11.95	16.89	29.05	46.52	V^0
	−1.5	2.7	30.4	18.4	23.5	25.6	25.8	α
SSC	27.08	36.83	—	—	—	28.58	—	V^0
	—	6.2	—	—	—	27.3	—	α
MODEL	27.08[1]	36.83[1]	13.31[2]	11.87[3]	16.49[3]	28.82[3]	46.05[3]	V^0
	.19	.47	.38	.37	.28	.22	.39	±
	1.0	6.2	23.6	23.4	24.3	24.7	26.1	α

1 from SSC; 2 this work; 3 average value & 1 standard deviation
BW: Bottinga and Weill (1970)
NC: Nelson and Carmichael (1970)
MCRS: Mo, Carmichael, Rivers and Stebbins (1982)
BWR: Bottinga, Weill and Richet (1982)
SCM: Stebbins, Carmichael and Moret (1984)
SSC: Stein, Stebbins and Carmichael (1984)

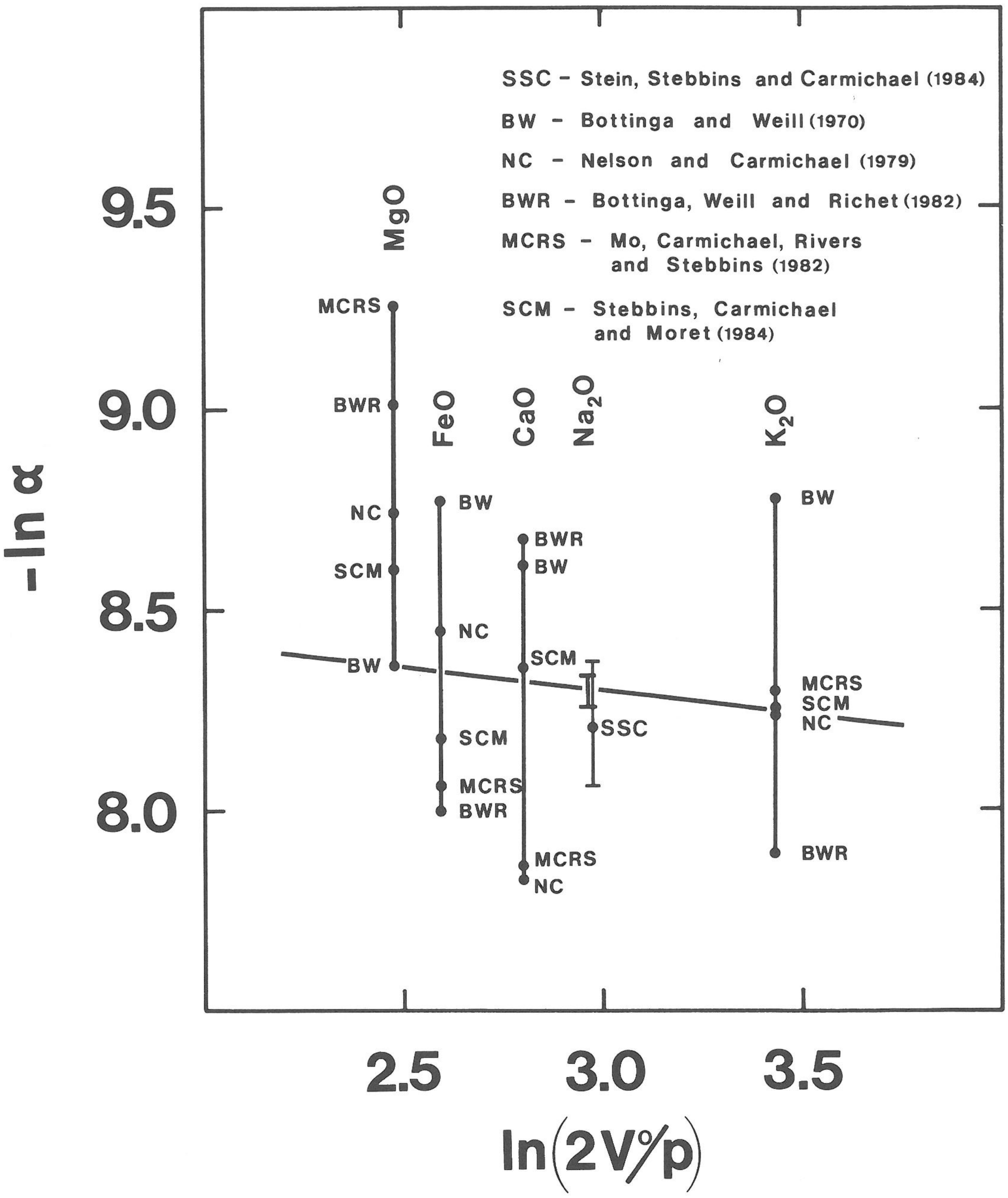

FIG. 1. Reported thermal expansivities of oxide components in silicate liquids (Table 2) and a recommended relation to specific volume.

shown are approximately the same. In light of these first order ambiguities, it is clear that the temperature derivative of the thermal expansivity for silicate liquids must be set at zero.

The pressure–volume relations were determined using a Birch-Murnaghan equation of state:

$$P = 3/2K\left\{\left[\frac{V(T,1)}{V(T,P)}\right]^{7/3} - \left[\frac{V(T,1)}{V(T,P)}\right]^{5/3}\right\} \times \left\{1 - 3/4(4-K')\left(\left[\frac{V(T,1)}{V(T,P)}\right]^{2/3} - 1\right)\right\} \quad (6)$$

where K is the isothermal bulk modulus at T and 1 atmosphere. K is calculated from the 1 atmosphere isothermal bulk modulus, K^0, at reference temperature, T_r, and known values for dK^0/dT; $K' = dK^0/dP$. Again, the reference temperature for crystals is 25°C. It is important to know the temperature derivative of the bulk modulus for the crystalline phases because these calculations are done at melting temperatures which are well in excess of room temperature where K^0 is usually determined for most minerals. Because this information is only rigorously known for forsterite, fayalite, and MgO, this fusion curve analysis is restricted to the olivines and β–quartz, where reasonable bounds can be inferred for the latter.

There is a considerable amount of ultrasonic information that indicates that the temperature derivative of the bulk modulus for silicate liquids is very small (RIVERS and CARMICHAEL, 1986; SATO and MANGHNANI, 1985), particularly above 1400°C; therefore, dK^0/dT for liquids has been set at zero.

In all cases, ΔS^0 was determined from the volume change of melting at 1 atmosphere and the initial slope, $(dT/dP)_i$, from the relation $\Delta S^0 = \Delta V(T_f, 1)/(dT/dP)_i$. The ΔS^0 for fayalite melting is in excellent agreement with the calorimetrically determined value from STEBBINS and CARMICHAEL (1984; see Appendix I). Calorimetric data are not available for forsterite melting. Inspection of Table 1 shows ΔS^0 to be much larger than that for fayalite melting. Although the initial slopes for both are similar, the difference arises because the volume change of melting of forsterite is much larger than that for fayalite. The ΔS^0 for β–quartz was determined from $\Delta V(T_f, 1)$ and the initial slope of metastable melting at 1 atmosphere as given by JACKSON (1976).

For fayalite melting, the calorimetric work of STEBBINS and CARMICHAEL (1984) was used to evaluated the entropy change above the 1 atmosphere melting temperature by the expression:

$$\int_{T_f}^{T}\frac{\Delta C_p dT}{T} = [(119.91T - 3.1167 \times 10^{-2}T^2 - 21057)/T]_{T_f}^{T}. \quad (7)$$

The same expression was used to determine the entropy change of forsterite melting above its 1 atmosphere melting temperature. However, it should be noted that these terms are very small and, indeed, could be dropped all together with only a trivial contribution to the overall error. For example, removing this term increases K^0 determined for Fe_2SiO_4 liquid from 33.0 GPa to 34.9 GPa.

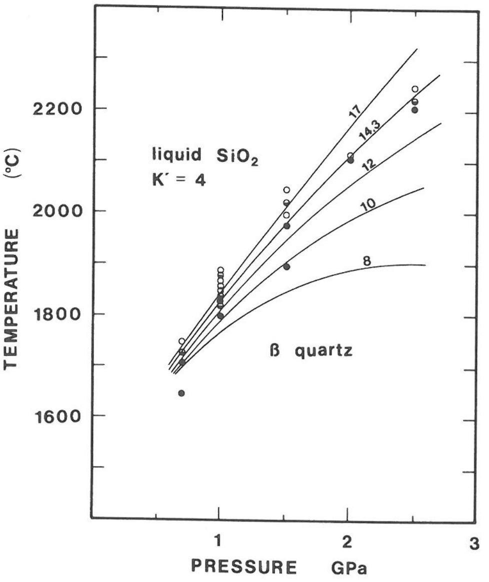

FIG. 2. Melting experiments on β–quartz (JACKSON, 1976) and simulated fusion curves for various values of K^0 for liquid SiO_2. Symbols: filled circles = β–quartz; open circles = glass. Thermal expansivity = 1.0×10^{-5}/°C.

Liquid SiO_2

Experimental data on the melting of β–quartz (JACKSON, 1976) are shown in Figure 2. Additionally, a number of simulated fusion curves are shown for SiO_2 liquid having a partial molar volume of 27.08 cm^3 (STEIN *et al.*, 1984) and a thermal expansivity of 1.0×10^{-5}/°C. The simulated fusion curve for an SiO_2 liquid having $K^0 = 14.3$ GPa is in very good agreement with the experimental data. An error in the bulk modulus of about ±2 GPa produces fusion curves which are resolvably at variance with the experimental data. In the hypothetical case of an SiO_2 liquid having $K^0 = 8$ GPa, the fusion curve is so strongly curved that dT/dP becomes zero at about 2.5 GPa, and SiO_2 liquid would have the same density as β–quartz.

A number of simulations were made in order to test the effect of uncertainties in the parameters on the derived bulk modulus. The results are:

a) Uncertainties in the partial molar volume of SiO_2 liquid at 1400°C result in an error which is small, and equivalent in size to those arising from the experimental data as shown by the range of values of Figure 3. This can be seen by comparing the bulk modulus of a STEBBINS *et al.* (1984) and a NELSON and CARMICHAEL (1979) SiO_2 liquid; the thermal expansivities of both are the same, but their partial molar volumes of 26.75 and 27.20 cm^3/gfw result in a bulk modulus of 21.8 and 20.1 GPa,

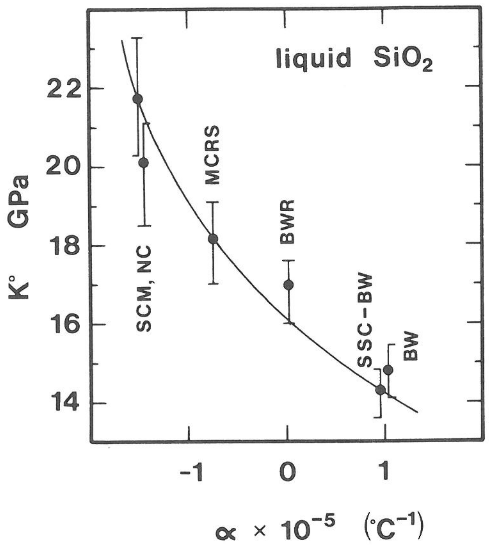

FIG. 3. The effect of thermal expansivity on the bulk modulus of liquid SiO_2 determined by a simulation of the observed melting experiments in the previous figure. See Figure 1 for key to acronyms.

respectively. A partial molar volume of 27.08 cm^3/gfw from STEIN *et al.* (1984) yields a molar volume of liquid Fe_2SiO_4 which is most consistent with the calorimetric and high pressure melting data for fayalite (Appendix I). Consequently, the STEIN *et al.* (1984) partial molar volume for liquid SiO_2 is used as the model value throughout this paper.

b) The largest uncertainties in the estimated bulk modulus of SiO_2 liquid arise from variations in the partial molar volume of SiO_2 liquid along the solidus at temperatures higher than 1400°C. This occurs because of published values of the thermal expansivity of SiO_2 liquid which range from -1.5 to $+1.0 \times 10^{-5}$/°C.

c) The ΔS^0 determined from the Clapeyron relation is about 8.7 J/gfw · °C. This value compares with 5.5 J/gfw · °C determined from the enthalpy measurements of RICHET *et al.* (1982). This smaller value is incapable of producing a simulated fusion curve which is consistent with the data of JACKSON (1976) under any condition; the $(dT/dP)_i$ is too high and the slope at higher pressures cannot be sufficiently lowered to conform with the experimental data. Because of this difficulty, ΔC_p was set at zero rather than computed from the equations in RICHET *et al.* (1982). The bulk modulus will be overestimated from this approximation by an amount which, judging from the calorimetry results for Fe_2SiO_4 liquid discussed below, is likely to be small.

d) Because there exists no direct measurements of dK^0/dT for quartz, its value was set at zero. It can be shown, however, that values which are larger in magnitude than -0.005 GPa/°C result in a simulated fusion curve for which d^2T/dP^2 becomes positive at pressures greater than about 3 GPa. This occurs largely because of the substantial reduction in the entropy change with increasing pressure. A bulk modulus of 14.3 GPa will be reduced to about 12.9 GPa for a hypothetical value of $dK°/dT = -0.004$ GPa/°C.

e) The effect of uncertainties in K' for liquid SiO_2 is demonstrated in Figure 4. The experimental data do not permit a unique value for K' to be determined. However, it is shown that for K' greater than or equal to 6, d^2T/dP^2 becomes positive in the metastable region at pressures around 5 GPa. A value of K' equal to 6 is likely to be an uppermost bound. For $K' = 4$, d^2T/dP^2 assumes its negative value throughout the stable and metastable regions.

Although there is a number of important uncertainties in this fusion curve analysis, the values of K^0 obtained for positive α (*i.e.*, about 14.3 GPa) are close to those which have been reported by other methods. In particular, BUCARO and DARDY (1976) measured the bulk modulus of amorphous SiO_2 between the glass transformation and melting temperatures of cristobalite by a light-scattering technique, and reported a value of 11.8 GPa. This result compares favorably with their interpretation of the data of WEINBERG (1962; 12.8 GPa), RENNINGER and UHLMANN (1974; 14.3 GPa) and the unpublished data of SCHOEDER quoted by BUCARO and DARDY (1976; 13.0 GPa). It is most likely that this

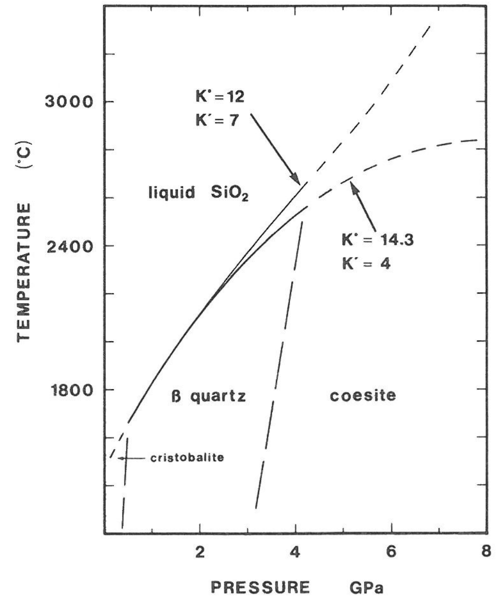

FIG. 4. Simulated fusion curves of β–quartz arising from $K' = 4$ to 7.

fusion curve analysis results in K^0 which is somewhat too high because of uncertainties (c) and (d) above. A thermal expansivity of 1×10^{-5}/°C yields a fusion curve-derived bulk modulus in closest agreement with those determined from other methods. The mean for K^0 from all methods of determination is 13 ± 1.3 GPa, a model value that will be adopted throughout the remainder of this paper.

Liquid Fe_2SiO_4

All experimental data on the melting of fayalite to high pressures are shown in Figures 5 and 6. These data are from three sources (LINDSLEY, 1967; AKIMOTO *et al.,* 1967; OHTANI, 1979) and are remarkably consistent. Melting at 1 atmosphere is incongruent, and becomes congruent at pressures between 1 atmosphere and 1.7 GPa (AKIMOTO *et al.,* 1967). The heat of melting for both congruent and incongruent melting at 1 atmosphere are nearly the same (STEBBINS and CARMICHAEL, 1984). Consequently, the simulations shown are valid for congruent melting at all conditions. The bulk moduli for the simulated fusion curves shown in Figures 5 and 6 are valid for the parameters listed in Table 1. As discussed more fully below, these are model parameters which were derived in order to develop an internally consistent set of thermodynamic and elastic properties for this system. A bulk modulus of 33 ± 2 GPa is obtained. A number of other simulations show that small deviations from 33 GPa result in simulated fusion curves that are in major violation of the experimental data.

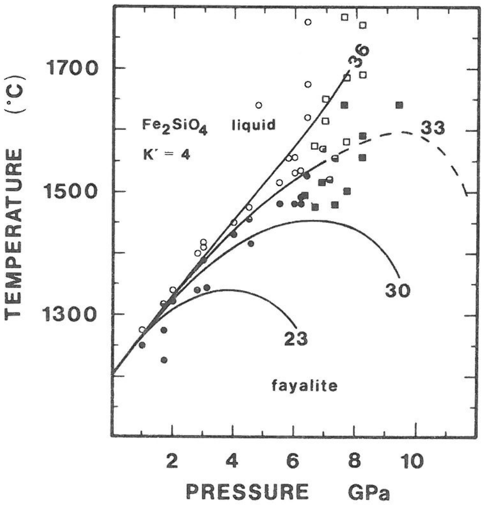

FIG. 5. Melting experiments on fayalite and simulated fusion curves for various values of K^0 for liquid Fe_2SiO_4. Symbols: filled circles = fayalite; open circles = quench fayalite; filled squares = spinel Fe_2SiO_4; open squares = quench spinel; other symbols are mixtures.

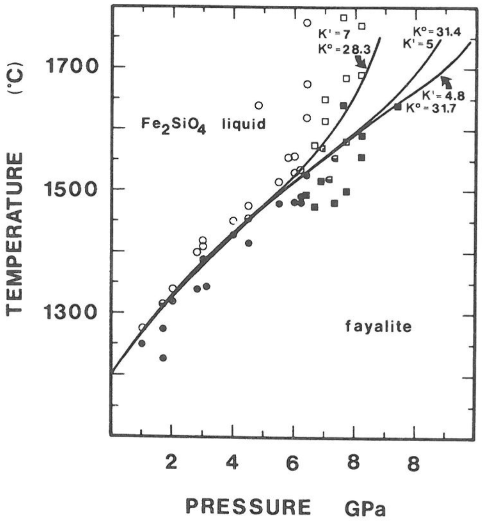

FIG. 6. Simulated fusion curves of fayalite arising from $K' = 4.8$ to 7. Symbols as for Figure 5.

Equally good simulations result from the raw data listed in Table 2 for liquid SiO_2 and FeO. However, the bulk modulus of liquid Fe_2SiO_4 ranges from about 44 GPa for the BOTTINGA and WEILL (1970; BW) parameters to about 25.6 GPa for a BOTTINGA *et al.* (1982; BWR) liquid (Figure 7), and depends largely on the value assumed for the thermal expansivity. The uncertainties in this analysis are small and arise from three sources, these being the initial slope (*i.e.*, $dT/dP_i = 68 \pm 2$°C/GPa), the experimental data that position the fayalite-spinel-liquid

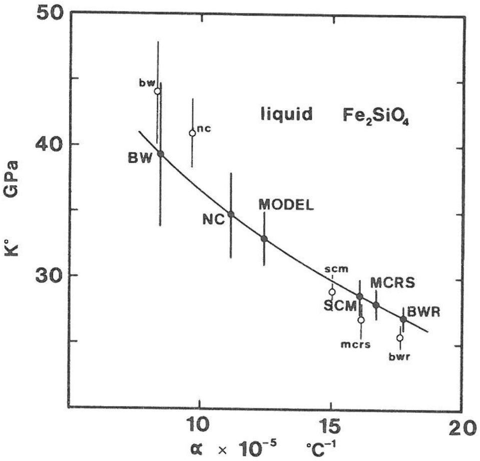

FIG. 7. K^0 vs thermal expansivity for liquid Fe_2SiO_4 determined from a fusion curve simulation of fayalite as a function of: A) volume and thermal expansivity of FeO and SiO_2 data reported in Table 2 (open circles, small lettering), and B) thermal expansivity of FeO, all other parameters kept constant (closed circles, large lettering). $K' = 4$. See Figure 1 for key to acronyms.

triple point at 1550° ± 10°C and 7 GPa, and a ±50°C error in temperature measurement at 7 GPa (OHTANI and KUMAZAWA, 1981).

It is clear that this or indeed any fusion curve analysis cannot yield a reliable value of the bulk modulus of the liquid phase in the absence of new constraints on the thermal expansivities of the liquid components. In the analysis which follows, improved constraints on the thermal expansivities for MgO and FeO indicate that there may be a regular and predictable relationship between thermal expansivity and specific volume, V_s. The specific volume is simply the volume per ion pair, defined as 2 (partial molar volume of i)/p, where p is the number of atoms per formula unit (ANDERSON; 1972). Its function is to permit an investigation of bulk-modulus-volume relations amongst materials having any number of atoms per formula unit (*e.g.*, ANDERSON and NAFE, 1965; ANDERSON, 1972). For many crystalline compounds a linear inverse relationship exists between the log of the bulk modulus and the log of volume, a relationship in which compression occurs according to an empirical law of corresponding states (ANDERSON, 1966). By analogy, it is suggested here that variations in thermal expansivity may also be related to specific volume. A relationship is shown in Figure 1 and arises largely from the new constraints for MgO and FeO discussed below; these thermal expansivities are very similar to that for Na_2O. The relationship shown in Figure 1 is a model which requires further testing. However, based on liquid MgO, FeO, and Na_2O it is suggested that there is no significant change in the thermal expansivity of a network modifying component in a silicate liquid with variations in the specific volume. From a survey of thermal expansivities for crystalline compounds, and metals in the liquid and solid states (HERZBERG, in preparation), it can be demonstrated that thermal expansivity varies positively with specific volume for the entire population of data. However, for any particular class of substances (*e.g.*, crystalline oxides, silicates, halides etc.) the variation is small or negligible. The model parameters of α for FeO, MgO, CaO, Na_2O, and K_2O listed in Table 2 were derived from Figure 1. Throughout the remainder of this analysis, a comparison will be made of these model expansivities and those reported for the raw experimental data.

Before we can proceed, there remains yet another problem concerning the choice of the correct value of the partial molar volume of FeO. Inspection of Table 2 shows that the range of published values is rather large (12.64 to 13.94 cm^3/gfw). Consequently, a model partial molar volume of FeO was determined (Appendix I), and has the value 13.31 ± 0.38 cm^3 at 1400°C.

The effect of thermal expansivity on the value of K^0 derived for Fe_2SiO_4 liquid was evaluated by keeping constant V^0 and α for SiO_2 and V^0 for FeO (*i.e.*, model values), and by using the range of reported thermal expansivities for FeO in Table 2. Simulation of the fusion curve of fayalite was repeated and the results are included in Figure 7. The uncertainties shown are from those listed above in addition to the partial molar volumes of liquid FeO and SiO_2 listed in Table 2. The results demonstrate unambiguously that the bulk modulus determined for liquid Fe_2SiO_4 depends mainly on the value assumed for the thermal expansivity of liquid FeO. The model molar volumes and thermal expansivities result in a bulk modulus of 33.0 ± 2.0 GPa.

The simulated fusion curves shown in Fig. 5 are valid for the model parameters of thermal expansivity and partial molar volumes discussed above with an additional restriction imposed; that is the pressure derivative of the bulk modulus is equal to 4. The effect of relaxing this restriction is shown in Figure 6. By increasing K' to 7, an upper bound for crystalline substances (ANDERSON, 1972), the simulated fusion curve is still consistent with the experimental data. However, the metastable extension inevitably develops the peculiar S-shape with d^2T/dP^2 becoming positive at high pressures. Because this configuration is contrary to all empirically determined fusion curves, it can be concluded that the high values of K' shown in Figure 6 must be in error. By trial and error it was determined that only those values of K' which are less than about 4.75 are capable of simulating a valid fusion curve, this being one in which d^2T/dP^2 is in all cases negative in both the stable and metastable regions.

Liquid Mg_2SiO_4

Experimental data on the melting of forsterite to high pressures are given in Figure 8, and originate from BOWEN and ANDERSEN (1914), DAVIS and ENGLAND (1964), and OHTANI and KUMAZAWA (1981). Again the interlaboratory agreement is excellent. Shown also are a number of simulated fusion curves having the model volume and thermal expansivity parameters listed in Tables 1 and 2, and the effect of varying the bulk modulus of Mg_2SiO_4 liquid. A value of K^0 = 35.0 ± 4.5 GPa is most consistent with the experimental data. Again, small deviations from this value result in a fusion curve which is resolvably at variance with the experimental data.

Bulk moduli obtained from use of the raw data in Table 2 are shown in Figure 9. The errors shown

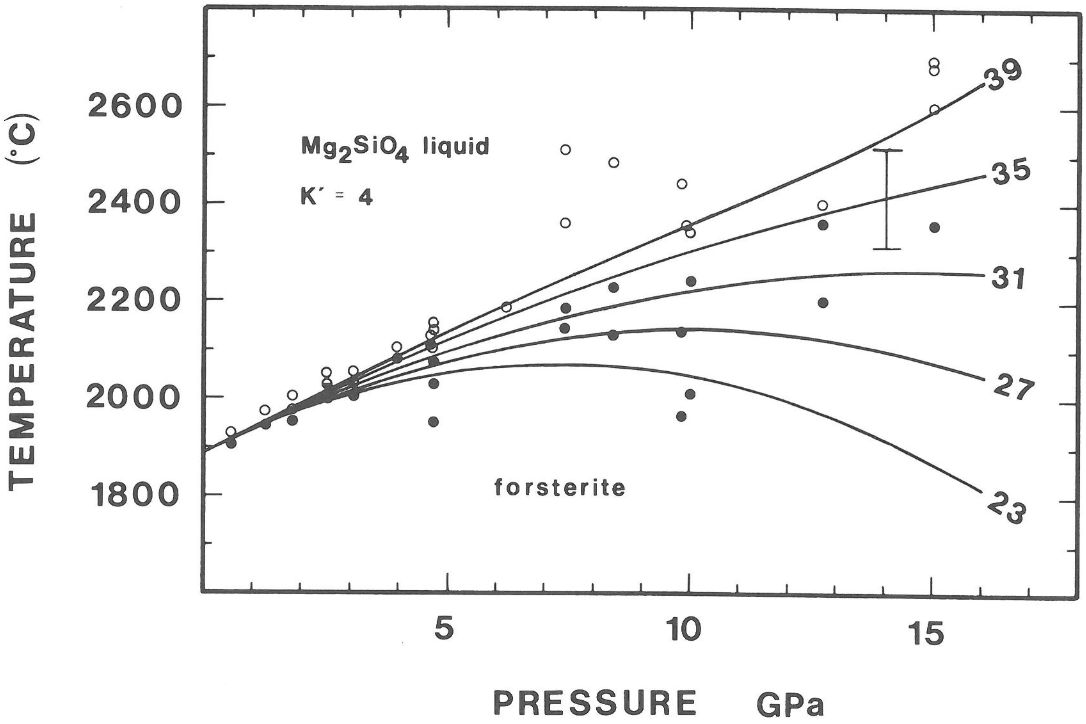

FIG. 8. Melting experiments on forsterite and simulated fusion curves for various values of K^0 for liquid Mg_2SiO_4. Symbols: filled circles = forsterite; open circles = quench forsterite.

are generated from uncertainties in the initial slope (55° ± 5°C/GPa) and temperature measurement at 14 GPa (±100°C; OHTANI and KUMAZAWA, 1981). As with liquid fayalite, the effects of uncertainties in the thermal expansivity of MgO was assessed by holding V^0 and α for SiO_2 constant, holding V^0 for MgO constant, and varying α for MgO; the results are included in Fig. 9. The model partial molar volume chosen for MgO is simply the mean of the reported range of values, and the errors arise from those described above in addition to the errors given for the partial molar volumes of MgO and SiO_2 in Table 2. A bulk modulus of 35.0 ± 4.5 GPa is calculated for the BOTTINGA and WEILL (1970) thermal expansivity and, as discussed below, is the model value chosen for liquid Mg_2SiO_4. Much higher values of the bulk modulus are derived for lower thermal expansivities, becoming as high as 55.1 ± 9.6 GPa. This is the main reason why the bulk modulus of the model Mg_2SiO_4 liquid derived in this fusion curve analysis is lower than those similarly derived by OHTANI (1984; 61.2 GPa) and BOTTINGA (1985; 58.8 GPa), although the choice of other parameters, particularly the temperature derivative of the thermal expansivity and bulk modulus for forsterite, also contribute to the differences. It is clear that the range of reported thermal expansivities for MgO can result in a calculated bulk modulus for liquid Mg_2SiO_4 which varies by over 200%.

Finally, bounds have been established on the pressure derivative of the bulk modulus, and the results are shown in Figures 10 and 11. Again high values of K' result in S-shaped fusion curves. By trial and error it was found that K' and K must be less than 4 and 35.0 GPa respectively.

COMPONENT OXIDE COMPRESSIBILITY IN SILICATE MELTS

In order to examine more clearly the effect of composition on the compressibility of silicate liquids, it is useful to have an algorithm wherein the bulk modulus of a complex liquid can be calculated from the bulk moduli of its constituent oxides. Although no general theory has been developed for silicate liquids, an analogous problem has been considered for mixtures of isotropic solids (WATT *et al.*, 1976) and for aqueous solutions in general (HAMANN, 1957; HAMMEL, 1985). Common to all these methods is that the bulk modulus of any complex substance K will be some function of the

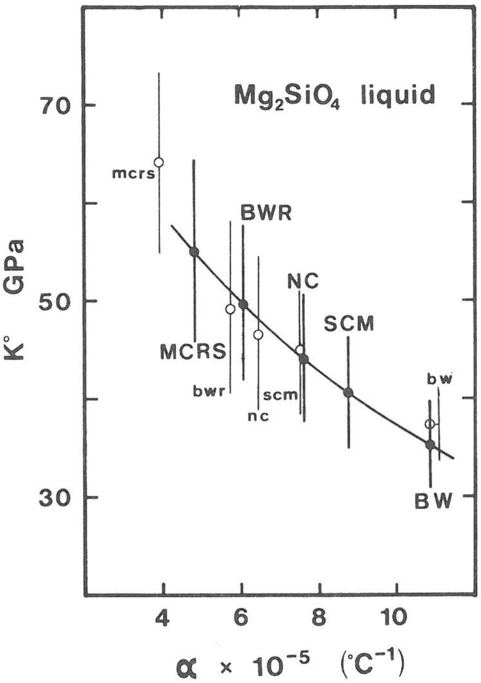

FIG. 9. K^0 vs thermal expansivity for liquid Mg_2SiO_4 determined from a fusion curve simulation of forsterite as a function of: A) volume and thermal expansivities of MgO and SiO_2 reported in Table 2 (open circles, small lettering), and B) thermal expansivity of MgO, all other parameters kept constant (closed circles, large lettering). See Figure 1 for key to acronyms.

bulk moduli of its components, K_i. These must be mixed in proportion to their volume fraction, V_i, not mol fractions, and thus are neither partial molar quantities nor extensive thermodynamic variables. For a Voigt average (*i.e.*, K_v):

$$K_v = \Sigma V_i K_i \tag{8}$$

and for a Reuss average (*i.e.*, K_r):

$$K_r = (\Sigma(V_i/K_i))^{-1}. \tag{9}$$

WATT *et al.* (1976) have demonstrated that the most satisfactory algorithm for reproducing experimental data on complex mixtures of isotropic crystalline substances from its endmember components is the average of the two, or the Voigt–Reuss–Hill (VRH) approximation:

$$K = (K_v + K_r)/2. \tag{10}$$

The application of the Voigt–Reuss–Hill mixing relation to silicate liquids is fraught with theoretical weaknesses which are revealed in some of the experimental studies discussed below. However, it is used in this analysis for want of a better algorithm, and because of its simplicity. Furthermore, it will be shown in Part 2 (HERZBERG, 1987) that it seems to be fairly successful in predicting the densities of complex melts which have been determined by independent methods.

Liquid FeO

With constraints now imposed on the bulk modulus of liquid Fe_2SiO_4 and SiO_2, K^0 for liquid FeO was calculated and the results are shown in Figure 12. The effect of uncertainties in thermal expansivity on the bulk modulus for liquid Fe_2SiO_4 (Figure 7) is propagated to liquid FeO, for which K^0 varies from about 54 to 100 GPa. The model thermal expansivity of liquid FeO yields a bulk modulus of 75.4 ± 9.0 GPa (Figure 12; Table 3).

Liquid MgO

The bulk modulus for liquid MgO was calculated from the range of possible values of the bulk modulus of liquid Mg_2SiO_4 and that for liquid SiO_2 (Figure 13). The calculations were done at 1400°C and 2825°C, the melting temperature of periclase, and the results are compared with the bulk modulus of crystalline MgO (SUMINO *et al.*, 1983). It can be seen that K^0 for liquid MgO ranges considerably, from about 90 to 170 GPa at 1400°C, and depends on the value assumed for the thermal expansivity of liquid MgO. At both temperatures, K^0 for MgO liquid having the thermal expansivities of MO *et al.* (1982; MCRS) and BOTTINGA *et al.* (1982; BWR) are higher than those for periclase. This, of course, is rather curious, implying that these thermal expansivities are in error. Only the BOTTINGA and WEILL (1970; BW) thermal expansivity and possibly that reported by STEBBINS *et al.* (1984; SCM) can provide a bulk modulus of liquid MgO that is smaller than that of periclase at 2825°C. Accordingly, these comparisons provide a new way of constraining the thermal expansivity of liquid MgO. Clearly, the value from BOTTINGA and WEILL (1970) must be preferred because all others predict a higher compressibility for crystalline MgO than liquid MgO, particularly at the melting temperature of periclase; accordingly the BOTTINGA and WEILL (1970) value is the model value chosen for liquid MgO.

The bulk modulus of liquid MgO at 1400°C which is preferred in this analysis is therefore 88.8 ± 19.2 GPa (Figure 13; Table 3). At 2825°C this becomes 75.8 ± 16.2 GPa, implying an apparent temperature derivative of −0.009 GPa/°C. This is

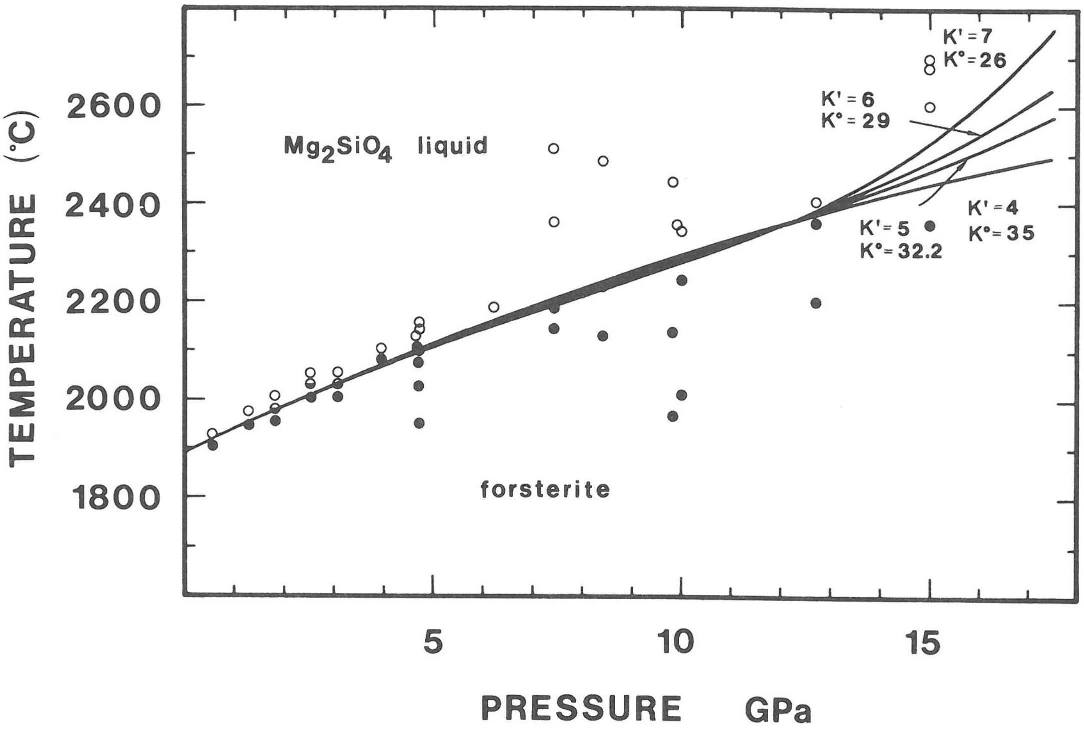

FIG. 10. Simulated fusion curves of forsterite arising from $K' = 4$ to 7. See Figure 8 for key to symbols.

not a true temperature derivative because it arises solely from the smaller volume fraction of the SiO_2 component in liquid Mg_2SiO_4 at 2825°C (*i.e.*, 0.465) compared to 1400°C (0.533).

Liquids of alkali oxides

A fairly thorough set of ultrasonic data is currently available on liquid compositions in the system MO–SiO_2 where MO is Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O (RIVERS and CARMICHAEL, 1986; BOCKRIS and KOJONEN, 1960; BAIDOV and KUNIN, 1968; and others), and the agreement amongst these

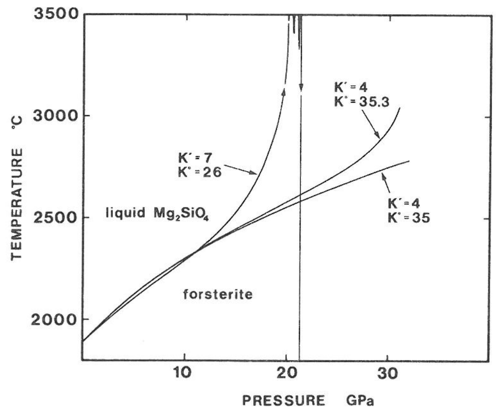

FIG. 11. Simulated metastable fusion curves of forsterite for various values of K'.

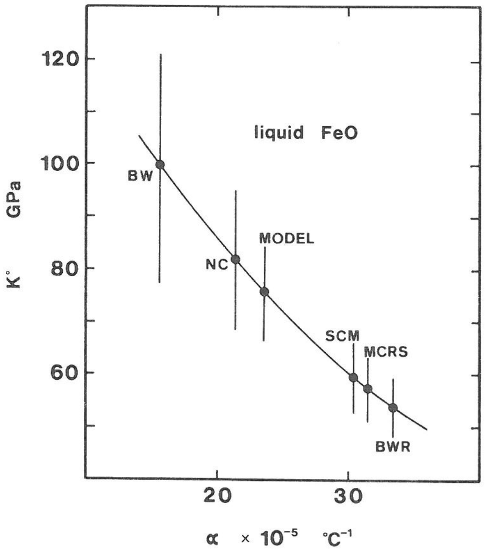

FIG. 12. K^0 for liquid FeO calculated from the bulk moduli of liquid Fe_2SiO_4 and SiO_2.

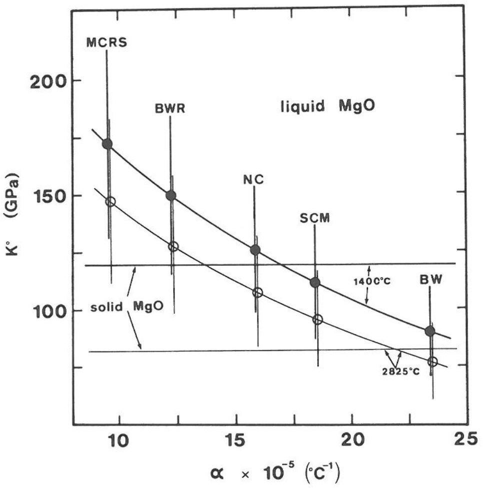

FIG. 13. K^0 for liquid MgO calculated from the bulk moduli of liquid Mg_2SiO_4 and SiO_2.

studies is generally very good (see RIVERS and CARMICHAEL, 1986, for detailed discussion). From the ultrasonic sound velocity, c, the adiabatic K_S and isothermal K_T bulk moduli are determined from the relations:

$$K_S = \rho c^2 \tag{11}$$

$$K_T = 1/(K_S^{-1} + T\alpha^2/\rho Cp) \tag{12}$$

where ρ is the density. For compositions on the join $MO-SiO_2$ α is determined from the thermal expansivities of the endmembers, α_i, (Table 2) by:

$$\alpha = \Sigma V_i \alpha_i. \tag{13}$$

The bulk thermal expansion coefficient is the summation of the end-member thermal expansivities mixed in proportion to their volume fractions. Values of Cp used in Equation (12) were taken from the partial molar heat capacities given in STEBBINS *et al.* (1984). The results of these calculations are very similar to those reported in RIVERS and CARMICHAEL (1986), the small differences reflecting slightly different values calculated for α. The results at temperatures close to or at 1400°C are shown in Figure 14.

An attempt has been made to model the data on these binaries using the Voigt–Reuss–Hill mixing relation, and the results are also shown (Figure 14). The solid curves are mixing lines between the alkali oxide end-members and SiO_2 at about 1400°C. The data on the join Li_2O-SiO_2 can be modelled reasonably well, but problems begin to arise with the system K_2O-SiO_2. Indeed, for all joins, there appears to be a "fine structure" in that the bulk modulus of the MO end-member seems to be bulk composition-dependent. When K^0 for SiO_2 is fixed at 13.0 GPa, the mixing line must be moved up and down in order to satisfy all the data on each binary. Such deviations from a simple Voigt–Reuss–Hill averaging scheme can also be seen in some liquid alloys in the systems Sb–Te and Bi–Te (GLAZOV *et al.*, 1983) and Mg–Bi, Sn–Bi and Sn–Pb (LYSOV and NOVIKOV, 1983). In these systems, the largest deviations of the data from the Voigt–Reuss–Hill equation occur for alloys having end-members which differ most in size and formal charge. Therefore, it is likely that this or indeed any other equation of the same form will only apply rigorously to mixtures having components which are structurally identical. The Voigt–Reuss–Hill approximation is, indeed, strictly an approximation. As discussed be-

Table 3. Isothermal bulk moduli (GPa) of oxide components in silicate liquids at 1400°C and 1 atmosphere

	K^0 *	Method of determination
SiO_2	13.0(1.3)	Light scattering & fusion curve
MgO	88.8(19.2)	Fusion curve—this work
	38.6(6.1)	Ultrasonic (K^0 for $MgSiO_3$ = 19.1; RIVERS and CARMICHAEL, 1986)
FeO	75.4(9.0)	Fusion curve—this work
	28.7(4.5)	Ultrasonic (K^0 for Fe_2SiO_4 = 19.3; RIVERS and CARMICHAEL, 1986)
CaO	49.4(5.4)	Ultrasonic (K^0 for $CaSiO_3$ = 22.9; RIVERS and CARMICHAEL, 1986)
SrO	43.1(7.9)	Ultrasonic (K^0 for $SrSi_2O_5$ = 18.7; RIVERS and CARMICHAEL, 1986)
BaO	34.6(6.1)	Ultrasonic (K^0 for $BaSi_2O_5$ = 18.1; RIVERS and CARMICHAEL, 1986)
Li_2O	26.8(12.2)	Ultrasonic (K^0 for Li_2O.24–SiO_2.76 = 14.8; BAIDOV and KUNIN, 1968)
Na_2O	13.5(3.0)	Ultrasonic (K^0 for $Na_2Si_2O_5$ = 13.2 GPa; RIVERS and CARMICHAEL, 1986)
K_2O	8.2(4.6)	Ultrasonic (K^0 for K_2O.12–SiO_2.88 = 11.9; BAIDOV and KUNIN, 1968)
Rb_2O	3.3(0.6)	Ultrasonic (K^0 for Rb_2SiO_5 = 7.2; RIVERS and CARMICHAEL, 1986)
Cs_2O	2.5(0.4)	Ultrasonic (K^0 for Cs_2SiO_5 = 6.0; RIVERS and CARMICHAEL, 1986)
Al_2O_3	20.9(4.5)	Ultrasonic (K^0 for $CaAl_2Si_2O_8$ = 20.0; RIVERS and CARMICHAEL, 1986)

* Except for SiO_2, oxide end-member values for K_0 were calculated from the mixture listed in Method of Determination and SiO_2 using Equation (10). Error is indicated in parentheses.

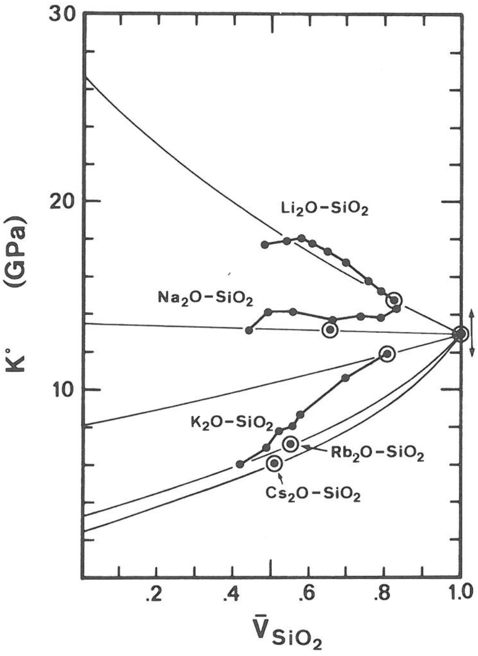

FIG. 14. Ultrasonic data on various liquid alkali oxide-SiO_2 binaries at $T = 1400°C$. Li_2O data from BAIDOV and KUNIN (1968; 1397°C); Na_2O data from BOCKRIS and KOJONEN (1960; 1300°C; circles), and RIVERS and CARMICHAEL (1986; 1420°C; dot-in-circle); K_2O data from BAIDOV and KUNIN (1968; 1397°C); Rb_2O and Cs_2O data from RIVERS and CARMICHAEL (1968; 1420°C). Solid curves are mixing lines between SiO_2 and the alkali oxide end-members listed in Table 3.

low, it will mask structural contributions to the elastic properties of silicate liquids.

With these mixing problems in mind, K^0 was calculated for each end-member using data from compositions closest to SiO_2. The philosophy behind this approach is that this should be most representative of the endmember bulk modulus of the alkali oxides in magmas occurring naturally; for all basic and ultrabasic compositions the concentrations are indeed small. Nevertheless, it should be noted that when the error in the bulk modulus of liquid SiO_2 is propagated in these calculations, K^0 for liquid Li_2O becomes valid for all data on the Li_2O–SiO_2 join. Similarly, K^0 for Na_2O should be valid for most of the Na_2O–SiO_2 binary if the spectrum of data at 1300°C (BOCKRIS and KOJONEN, 1960) can be shifted to the 1420° data point of RIVERS and CARMICHAEL (1986). However, an error propagation cannot satisfy the high potassium data on the join K_2O–SiO_2. Consequently, K^0 for liquid K_2O calculated for the silica-rich compositions will be higher than those for the K_2O-rich composition. The same problem is encountered for compositions on the joins Rb_2O–SiO_2 and Cs_2O–SiO_2 (RIVERS and CARMICHAEL, 1986) where even larger differences exist in the SiO_2-molar volumes of these endmembers. For these the bulk modulus will probably be considerably underestimated compared to compositions on those joins which are more SiO_2-rich, and this is revealed again in the analysis which follows.

For the Rb_2O and Cs_2O compositions studied by RIVERS and CARMICHAEL (1986), it should be noted that K^0 for these end-members can only have positive values when derived from the Voigt–Reuss–Hill or the Reuss approximations. Negative values are obtained when the endmembers are mixed either by volume using the simple Voigt scheme or by mol fractions. The results of these mixing calculations are summarized in Table 3.

Liquids of the alkali earth oxides

The bulk moduli of liquids CaO, SrO, and BaO were similarly calculated from the ultrasonic data of RIVERS and CARMICHAEL (1986) for the compositions $CaSiO_3$, $SrSi_2O_5$, and $BaSi_2O_5$ (Table 3). The value for CaO may be slightly lower than the desired value at 1400°C because the ultrasonic data for $CaSiO_3$ was obtained at 1563°C.

DISCUSSION OF RESULTS

The bulk moduli of the components in silicate liquids listed in Table 3 have been plotted in Figures 15 and 16. These are compared with elastic data for crystalline binary compounds, crystalline metals,

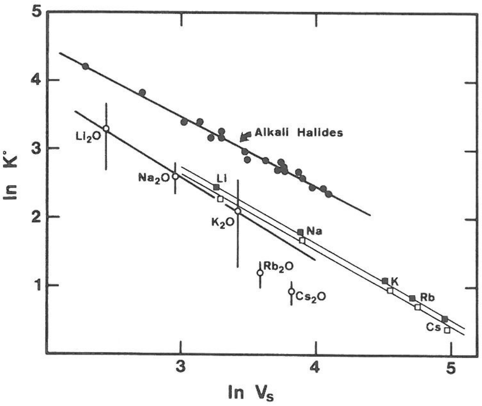

FIG. 15. The empirical law of corresponding states observed for: crystalline alkali halides (closed circles; Table AII–2); crystalline alkali metals (closed squares; Table AII–1) and liquid alkali metals (open squares; Table AII–1) in Group IA; and liquid alkali oxides of cations in Group IA (open circles) determined from Figure 14, with errors arising from uncertainties in K^0 for SiO_2.

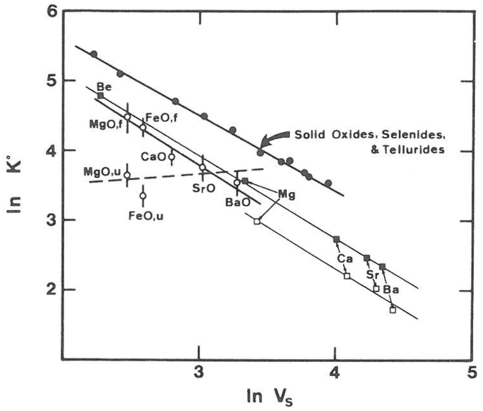

FIG. 16. The law of corresponding states observed (solid lines) for crystalline binary compounds having cations in Group IIA (closed circles; Table AII–2), crystalline metals (closed squares; Table AII–1) and liquid metals (open squares; Table AII–1) in Group IIA. For liquid oxides (open circles) the law of corresponding states is observed for MgO,f and FeO,f deduced from the fusion curve analysis, and violated (broken line) for MgO,u and FeO,u deduced from ultrasonic data.

and liquid metals in Groups IA and IIA of the periodic table listed in Appendix II. As noted above, there is a well-known regular and inverse relationship between the log of the bulk modulus and the log of the specific volume for a wide range of binary crystalline substances (ANDERSON and NAFE, 1965; ANDERSON and ANDERSON, 1970; ANDERSON, 1972), particularly those belonging to the same group in the periodic table. This relationship takes the form:

$$\ln K^0 = s \ln V_s + C \tag{14}$$

where the slope, s, has a remarkably constant value of about -1 for most crystalline binary compounds. ANDERSON (1966) proposed that these substances compress in observation of the empirical law of corresponding states, in which the bulk modulus can be determined solely by the specific volume. The data in the original Anderson compilations have been updated, and are listed in Appendix II. Additionally, a large amount of ultrasonic data is now available on the elastic properties of liquid metals, and these have also been compiled in Appendix II.

The data in Figure 15 are restricted to substances of the monovalent cations in Group IA. Although the error is fairly large, there is a clear inverse relationship between bulk modulus and specific volume for liquid Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O. Using the linear least squares regression method of YORK (1966) for five data points, Equation (14) becomes:

$$\ln K^0 = -1.82(0.21) \ln V_S + 7.940(0.85). \tag{15}$$

It was noted above, however, that K^0 for Rb_2O and Cs_2O are probably underestimated compared to those for more silica-rich compositions on the joins Rb_2O–SiO_2 and Cs_2O–SiO_2. By regressing only the data for Li_2O, Na_2O, and K_2O, the parameters in Equation (14) become: $s = -1.22(0.05)$ and $C = 6.24(0.14)$; the Rb_2O and Cs_2O data plot well below the line as anticipated. For the crystalline alkali halides in Appendix II, $s = -1.02(0.03)$ and $C = 6.55(0.26)$. These results suggest that there may be a relationship between compounds in the liquid and crystalline states; the constant C in Equation (14) may be similar but the slope s may always be larger for liquids compared to crystals. This, however, is not definitive at the present time because the errors in the regressions are fairly large.

The bulk moduli for liquid oxides of cations in Group IIA (Table 3) are plotted in Figure 16; the results for liquid FeO are included. Two possible linear regressions can be entertained. For MgO and FeO determined from the fusion curve analysis, together with the results for CaO, SrO, and BaO inferred from ultrasonic data, the regression is semi-parallel to the data for crystalline binary compounds and metals in the liquid and crystalline states; the regression yields $s = -1.23(0.12)$ and $C = 7.48(0.44)$. For crystalline binary compounds $s = -1.09(0.02)$ and $C = 7.78(0.14)$, again suggesting that C may be constant for all liquid and crystalline binary compounds having cations in Group IIA.

The other possible regression is very different. By using K^0 for MgO and FeO inferred from the ultrasonic data of RIVERS and CARMICHAEL (1986) for liquid $MgSiO_3$ and Fe_2SiO_4, respectively (see Table 3), the inverse relationship between K^0 and V_s seen for all other systems no longer holds. There appears to be no volume dependence to the bulk modulus and the law of corresponding states seems to be violated; a regression yields $s = +0.16(0.49)$ and $C = 3.20(1.83)$ with substantial errors.

Before the apparent violation of the law of corresponding states is discussed, it is useful to complete this survey by considering K^0 for liquid Al_2O_3. This was determined from the bulk modulus of liquid anorthite (RIVERS and CARMICHAEL, 1986), liquid SiO_2 (Table 3), and liquid CaO calculated from the regression for which the law of corresponding states applies. The bulk modulus of liquid Al_2O_3 is 20.9 ± 4.5 GPa (Table 3). This value is consistent with 25.0 GPa determined from an extrapolation of the ultrasonic velocity data of SLAGLE and NELSON (1970) to 1400°C. This value is plotted (Figure 17) together with other substances that have a mean atomic weight of about 20. ANDERSON

(1972) showed that this is a special case of the law of corresponding states, equivalent to Birch's Law, in which the slope of the regression for the crystalline oxides is now close to −4. A very similar relationship is apparent for the liquid oxides as well. It should be noted that a much better fit for liquid MgO, Al_2O_3 and SiO_2 could be obtained if the bulk modulus of anorthite liquid (RIVERS and CARMICHAEL, 1986) is slightly underestimated; that is, large underestimates of K^0 for liquid Al_2O_3 accrue from minor underestimates of K^0 for liquid $CaAl_2Si_2O_8$.

A single equation is all that is needed to describe fully bulk modulus–volume relations for crystalline alkali halides of cations in Group IA in addition to crystalline oxides, tellurides, and selenides of cations in Group IIA (see listing of these in Table AII–2); that is, it seems to be independent of the nature of the anion. Similarly, the law of corresponding states holds rigorously for crystalline metals in Group IIA. These relations are quite remarkable, and imply the existence of a simple elastic law which describes each crystalline binary metal–anion system and its intermediate compounds. With the law of corresponding states firmly established for liquid metals as well (see Figures 15, 16, and AII–1), a similar law is anticipated for liquids in any metal–anion binary system containing intermediate compounds. This is clearly indicated for all the liquid oxide components which include MgO and FeO determined from the fusion curve analysis. However, K^0 for these deduced from the ultrasonic measurements of RIVERS and CARMICHAEL (1986) on $MgSiO_3$ and Fe_2SiO_4 (see Table 3) are inconsistent with these laws. The K^0 for liquid Fe_2SiO_4 from the ultrasonic data is 19.3 GPa; inspection of Figures 5 and 6 demonstrates that the high pressure melting experiments on fayalite are inconsistent with this. Similarly, by using K^0 for liquid MgO determined from the ultrasonic data for $MgSiO_3$, K^0 for liquid Mg_2SiO_4 can be calculated to be 21.9 ± 2.1 GPa. Inspection of Figures 8 and 10 shows that the ultrasonic data are also inconsistent with the melting data on forsterite. Clearly, additional data would be useful in order to resolve the contradictory results for liquid compositions that are enriched in MgO and FeO.

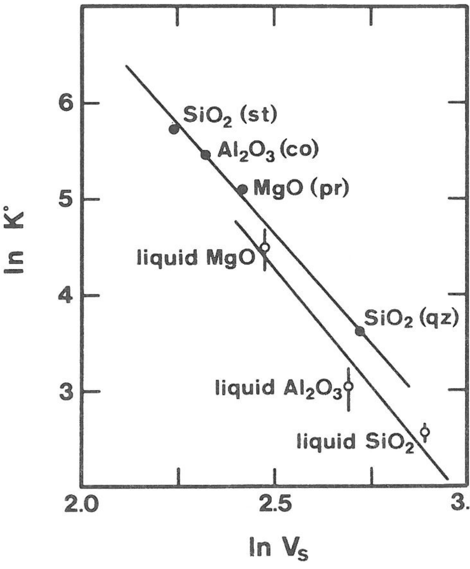

FIG. 17. Birch's Law observed for both liquid and crystalline oxides having similar mean atomic weights (≈20), with liquid MgO deduced from the fusion curve analysis. Data for stishovite, quartz, and periclase from WEIDNER *et al.* (1982), LEVIEN *et al.* (1980), and SUMINO *et al.* (1983) respectively.

For melts of geological interest that can have a variable MgO content (*e.g.*, basalts-komatiites) the effect of composition on compressibility is most clearly seen in Figure 17 where major differences in K^0 amongst MgO, Al_2O_3, and SiO_2 are demonstrated. Because MgO is a network modifier and the others are network formers, the simplest interpretation is that there is a structural control to the bulk modulus of silicate liquids, and this is reflected in Birch's Law. In crystals, glasses, and melts, the Si–O bond length is remarkably constant for a whole range of compositions (NAVROTSKY *et al.*, 1985), suggesting that the high bulk modulus of individual SiO_4 tetrahedra in crystals (*e.g.*, LEVIEN *et al.*, 1980; HAZEN and FINGER, 1979) is valid for liquids and glasses as well. However, in addition to reductions in the metal-oxygen bond length, it is the way in which SiO_4 and other polyhedra are structurally arranged that determines the aggregate compression of crystalline materials (HAZEN and FINGER, 1979), and this is best demonstrated by the low bulk modulus for quartz (LEVIEN *et al.*, 1980). For liquid compositions enriched in SiO_2, the high compressibility is most probably accomodated by the tilting or kinking of corner-sharing tetrahedral linkages, rather than any shortening in the Si–O bond length as is the case for quartz. However, crystalline MgO is relatively incompressible because it has a sodium chloride structure in which the MgO_6 octahedra share triangular faces. Opportunities for interpolyhedral bond angle distortion are minimized and compression is taken up largely by a reduction in the length of the Mg–O bond. Because liquid MgO is the most incompressible of all the liquid oxides considered, it can be inferred that it compresses in much the same way. Therefore, for complex liquids on the join $MgO–SiO_2$, it is suggested that the bulk modulus becomes reduced with increasing SiO_2

content because the mechanism of compression changes from intrapolyhedron bond length shortening to interpolyhedron bond angle distortions. In detail, however, this interpretation is bound to be a gross oversimplification because it ignores any possible effects arising from structural complexities in both short and intermediate range ordering; examples are the possibility of tetrahedrally coordinated Mg (YIN *et al.,* 1983) and various possible anionic configurations (*e.g.,* monomers, chains, rings etc.; MYSEN *et al.,* 1982). If the effects of these structural changes on bulk modulus are measurable by experiment, they will most certainly be manifest as a fine structure superimposed on the Voigt–Reuss–Hill relation or, indeed, any other mixing approximation.

CONCLUSIONS

From an analysis of the fusion curves for β–quartz, forsterite, and fayalite in addition to light scattering and ultrasonic measurements on silicate liquids, the following conclusions have been drawn:

a) The bulk moduli for liquid SiO_2, Fe_2SiO_4, and Mg_2SiO_4 retrieved from any fusion curve analysis depend critically on the choice of suitable values of the thermal expansivities of these liquids. Accordingly, constraints have been provided on the wide range of values reported for the thermal expansivity of silicate liquids; the thermal expansivities for all components other than the network formers SiO_2 and Al_2O_3 appear to be largely independent of composition.

b) The pressure derivative of the bulk modulus, K', must be less than 6, 4.7, and 4 for liquid SiO_2, Fe_2SiO_4 and Mg_2SiO_4 respectively. It is suggested that K' for liquids and crystals of the same composition are similar, and that the very high values estimated by OHTANI (1984; 5.5 to 6.6 for liquids having the compositions of fayalite, pyroxenes, and garnets) and BOTTINGA (1985; 9.79 to 23.33 for liquids having compositions of pyroxene, garnets and albite) could be an artifact of the choice of parameters they used. In particular, the proper values of the thermal expansivity of the liquid phase, and temperature derivatives of the thermal expansivity and bulk modulus of the crystalline phases are essential; the latter have only been well characterized for MgO, Mg_2SiO_4, and Fe_2SiO_4.

c) The K^0 for liquid SiO_2 is in good agreement with that determined by light scattering methods. However, K^0 for liquid Fe_2SiO_4 and Mg_2SiO_4 are much higher than those obtained or deduced from the ultrasonic data of RIVERS and CARMICHAEL (1986).

The bulk modulus of the oxide components SiO_2, Al_2O_3, FeO, MgO, CaO, SrO, BaO, Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O in silicate liquids at 1400°C have been estimated. For liquid MgO and FeO which have been deduced from an analysis of the fusion curves of forsterite and fayalite, there is an inverse relationship between K^0 and the specific volume. ANDERSON (1966) noted that this relationship applies to crystalline binary compounds, and proposed that these substances compress according to the law of corresponding states. It is demonstrated that this elastic law applies also to liquid and crystalline metals. However, K^0 for liquid MgO and FeO which have been deduced from the ultrasonic data of RIVERS and CARMICHAEL (1986) on liquid $MgSiO_3$ and Fe_2SiO_4 contradict the law of corresponding states, demonstrating that either the law is not universal or the data are erroneous. Additional experimental data on silicate liquids having high MgO and FeO are needed to resolve these contradictions.

RIGDEN *et al.* (1984) concluded that silicate melts will be denser than olivine in the 6 to 10 GPa range. This was based on the assumption that the effect of composition on the bulk modulus of silicate liquids is small. At the time, this conclusion was certainly justified because the bulk modulus of their basalt analogue $An_{36}Di_{64}$ is so similar to that reported by RIVERS and CARMICHAEL (1986) for liquid Fe_2SiO_4. However, it has been shown that the RIVERS and CARMICHAEL (1986) determination is inconsistent with K^0 derived from an analysis of the melting curve of fayalite; it also contradicts the inverse relationship between K^0 and specific volume embodied in the law of corresponding states. The hypothesis of olivine flotation in ultrabasic magmas at high pressures is thus based upon an assumption of questionable merit. A universal elastic law has geological consequences on olivine-magma density relations in the upper mantle which are profoundly different from a law that is violated. These possibilities are explored in Part 2 (HERZBERG, 1987).

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APPENDIX I

The wide range of reported values for the partial molar volume of liquid FeO (Table 2) are propagated to important uncertainties in the molar volume of Fe_2SiO_4 used in the fusion curve analysis. Accordingly, an independent method for determining the partial molar volume of FeO was developed and is discussed here. In Table AI–1 are listed the molar volumes at 25°C and 1 atmosphere for a wide range of different phases having compositions which are pure Mg and Fe end-members. These have been plotted in Figure AI–1. The data were obtained from Table 1, ROBIE *et al.* (1966, 1978), JEANLOZ and THOMPSON (1983), and HELGESON *et al.* (1978). It can be seen that an extremely good correlation exists, and this must be attributed to the different sizes of the Fe and Mg cations. A regression of the data yields:

$$V^0, \text{Fe phase} = 1.022\,(V^0, \text{Mg phase}) + 0.760 \qquad \text{(AI–1)}$$

with a correlation coefficient of .99989.

The partial molar volume of liquid MgO was determined at 25°C from its model partial molar volume at 1400°C and model α in Table 2. By using Equation (AI–1) the partial molar volume of liquid FeO at 25°C was determined, then extended back to 1400°C using model α in Table 2 for liquid FeO, and yields 13.31 ± 0.38 cm^3/gfw. This is close to the average of the values reported for liquid FeO in Table 2.

Constraints on the correct value for the partial molar volume of liquid FeO can also be evaluated using the experimental data of HERZBERG *et al.* (1982) on the join forsterite–fayalite. For a wide range of intermediate compositions on this join the liquids are more dense than coexisting olivines because of the extensive partitioning of the heavier element Fe into the liquid phase. It was demonstrated by experiment that for the bulk composition forsterite$_{30}$–fayalite$_{70}$ (mol percent) at 1425°C and 1 atmosphere, olivine ($Fo_{58.5}$) floats on its coexisting liquid ($Fo_{24.2}$). We now examine which of the reported values of V^0 for liquid FeO in Table 2 are consistent with these experimental observations.

From the raw data in Table 2 and the equation of state parameters for olivine derived from the forsterite and fayalite end-members in Table 1 (see Part 2, this volume) it can be demonstrated that only the data of BOTTINGA and WEILL (1970; BW), NELSON and CARMICHAEL (1979; NC), and STEBBINS *et al.* (1984; SCM) predict olivine floatation. The data of BOTTINGA *et al.* (1982; BWR) and MO

Table AI–1. Molar volumes of Mg and Fe phases at 25°C and 1 atmosphere

	V^0 Mg-phase (cm^3/gfw)	V^0 Fe-phase (cm^3/gfw)
(Mg, Fe)O	11.25	12.25
(Mg, Fe)$_2$SiO$_4$ α	43.63	46.26
(Mg, Fe)$_2$SiO$_4$ β	40.52	43.22
(Mg, Fe)$_2$SiO$_4$ γ	39.65	42.02
(Mg, Fe)SiO$_3$ opx	31.33	32.96
(Mg, Fe)SiO$_3$ pv	24.46	25.49
(Mg, Fe)SiO$_3$ il	26.35	26.85
Ca(Mg, Fe)Si$_2$O$_6$	66.09	68.27
K(Mg, Fe)(Si$_3$AlO$_{10}$)(OH)$_2$	149.66	154.32
(Mg, Fe)Al$_2$O$_4$	39.71	40.75
(Mg, Fe)$_3$Al$_2$Si$_3$O$_{12}$	113.29	115.28
(Mg, Fe)TiO$_3$	30.86	31.71
(Mg, Fe)CO$_3$	28.02	29.38
(Mg, Fe)Cr$_2$O$_3$	43.56	44.01
(Mg, Fe)$_5$Al(Si$_3$AlO$_{10}$)(OH)$_8$	207.11	213.42
7A(Mg, Fe)$_5$Al(Si$_3$AlO$_{10}$)(OH)$_8$	211.5	221.2
Na$_2$(Mg, Fe)$_3$Fe$_2$Si$_8$O$_{22}$(OH)$_2$	271.3	274.9
NaCa$_2$(Mg, Fe)$_4$Fe(Si$_6$Al$_2$O$_{22}$)(OH)$_2$	273.8	280.3
NaCa$_2$(Mg, Fe)$_4$Al(Si$_6$Al$_2$O$_{22}$)(OH)$_2$	273.5	279.9

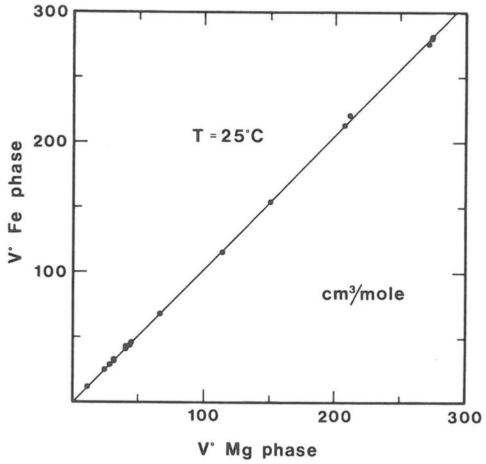

FIG. AI-1. Molar volumes of a wide range of Fe and Mg phases listed in Table AI-1.

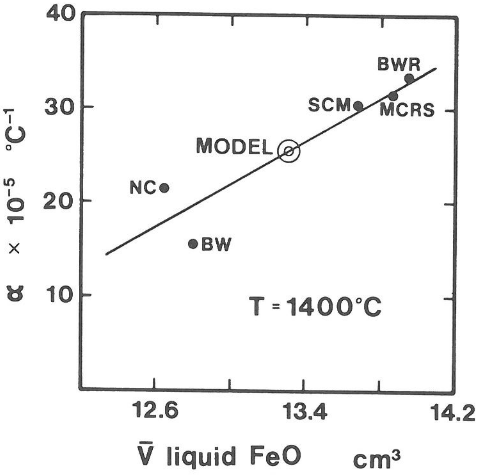

FIG. AI-3. Thermal expansivities and partial molar volumes of liquid FeO reported in Table 2.

et al. (1982; MCRS) yield the opposite result, predicting olivine denser than its coexisting liquid.

These calculations are now repeated keeping the volumes of the liquid components SiO_2 and MgO constant (*i.e.*, the model parameters in Table 2), and varying V^0 and α for liquid FeO according to the raw and model parameters. The results are shown in Figure AI-2. It can be seen that only the model parameters for V^0 and α, in addition to those of NELSON and CARMICHAEL (1979; NC) and BOTTINGA and WEILL (1970; BW), are consistent with the experimental results. It is concluded that V^0 and α for liquid FeO reported by MO *et al.* (1982), BOTTINGA *et al.* (1982), and STEBBINS *et al.* (1984) are in error.

The range of reported values for α and V^0 for liquid FeO in Table 2 are shown in Figure AI-3. It appears that

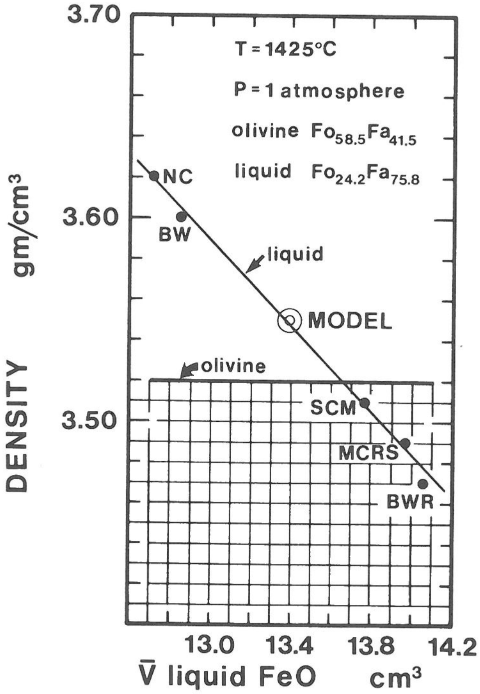

FIG. AI-2. Computed densities of olivine crystals and coexisting liquid for an experiment in the system forsterite–fayalite at 1 atmosphere where olivine flotation has been documented (HERZBERG *et al.*, 1982). Data of SCM, MCRS, and BWR in the hatched region are inconsistent with the experimental observation of olivine flotation.

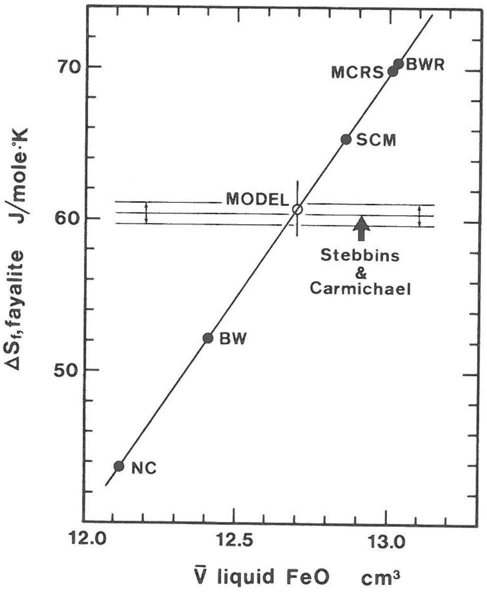

FIG. AI-4. Entropy of fusion of fayalite at 1 atmosphere determined calorimetrically (STEBBINS and CARMICHAEL, 1984) and computed using the volume data for FeO as shown. Only the Model V^0 and α for liquid FeO are in agreement with the calorimetric data.

a correlation exists, suggesting that experimental errors in the determination of the two are coupled. Regressing the raw data yields a value for α which is $25.6 \times 10^{-5}/°C$ for liquid FeO having $V^0 = 13.31$ cm^3/gfw, in excellent agreement with the model value in Table 2.

From the fusion curve data of fayalite (Figures 5 and 6) an initial slope of 68 ± 2°C/GPa is tightly constrained; with slopes outside of these bounds it is difficult to simulate the high pressure melting experiments with any combination of adjusted values of K^0 and K' for liquid Fe_2SiO_4.

Table AII–1. Specific volumes and isothermal bulk moduli for liquid and crystalline metals and nonmetals

	V_s 2x (cm^3/gfw)	K^0 (GPa)	Reference
Li, l	26.85	9.80	1, 2
Li, c	26.04	11.55	3
Na, l	49.61	5.38	4
Na, c	47.48	6.04	3
K, l	94.94	2.62	4
K, c	91.12	2.97	3
Rb, l	115.89	2.03	4
Rb, c	111.48	2.30	3
Cs, l	144.46	1.45	4
Cs, c	140.80	1.71	3
Be, c	9.77	119.0	5
Mg, l	30.59	19.8	6, 9
Mg, c	27.99	35.6	7
Ca, l	59.38	9.1	6, 9
Ca, c	54.37	15.5	8
Sr, l	73.79	7.6	6, 9
Sr, c	68.28	11.8	8
Ba, l	82.93	5.6	6, 9
Ba, c	76.41	10.5	8
Al, l	22.58	52.1	6, 10
Al, c	20.01	72.6	11
Ga, l	23.63	44.2	6, 12
Ga, c	23.59	58.0	8
In, l	32.74	33.5	6, 12
In, c	31.52	39.6	13
Tl, l	36.43	26.1	6, 4, 12
Tl, c	34.49	36.4	8, 14
C, diamond	6.84	442.0	15, 16
Si, l	22.20	78.7	17
Si, c	24.10	96.1	18
Ge, l	26.35	46.5	17
Ge, c	27.26	74.2	18
Sn, l	34.06	36.9	4
Sn, c	32.59	54.2	14

l = liquid; c = crystalline.

1 McALISTER *et al.* (1976). 2 GOL'TSOVA (1966). 3 SWENSON (1985). 4 WEBBER and STEPHENS (1968). 5 MING and MANGHNANI (1984). 6 CRAWLEY (1974). 7 ROMAIN *et al.* (1976). 8 GSCHNEIDNER (1964). 9 McALISTER *et al.* (1974). 10 TSU *et al.* (1982). 11 TALLON and WOLFENDEN (1979). 12 isothermal bulk modulus calculated from adiabatic data in PASHUK and PASHAEV (1983) with heat capacity and thermal expansivity parameters in 4 and 6. 13 MADHAVA and SAUNDERS (1979). 14 GERWARD (1985). 15 McSKIMIN *et al.* (1972). 16 GRIMSDITCH and RAMDAS (1975). 17 theory from SHIH and STROUD (1985). 18 GONCHAROVA *et al.* (1983).

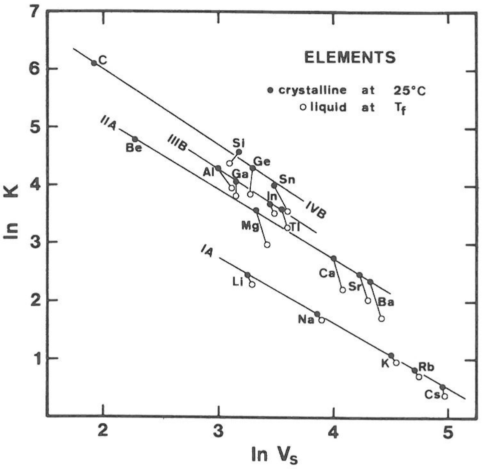

FIG. AII–1. The law of corresponding states observed for both liquid and crystalline metals and nonmetals occupying Groups IA, IIA, IIIB, and IVB of the periodic table.

Table AII–2. Specific volumes and isothermal bulk moduli of crystalline binary compounds at 25°C

	V_s (cm^3/gfw)	K^0 (GPa)	Reference
LiF	9.84	66.51	1
LiCl	20.45	29.68	1
LiBr	25.07	23.52	1
LiI	32.73	17.26	1
NaF	14.99	46.48	1
NaCl	27.02	23.68	1, 2
NaBr	32.17	19.47	1
NaI	40.83	14.87	1
KF	23.04	30.22	1
KCl	37.51	17.35	1
KBr	43.30	14.64	1
KI	53.13	11.51	1
RbF	27.19	26.68	1
RbCl	42.94	15.58	1
RbBr	49.26	13.24	1
RbI	59.60	10.49	1
CsCl	42.19	16.69	3
CsBr	47.75	14.57	3
CsI	57.40	11.56	3
BeO	9.30	220.1	4
MgO	11.25	162.8	5
CaO	16.76	11.2	6
SrO	20.69	89.28	6
BaO	25.59	74.06	6
CaSe	31.30	52.0	7
SrSe	36.68	46.7	7
BaSe	43.28	39.6	7
CaTe	38.66	47.4	7
SrTe	44.47	37.0	7
BaTe	51.65	34.1	7

1 SMITH and CAIN (1975). 2 BOEHLER and KENNEDY (1980). 3 SUMINO and ANDERSON (1984; averages at 25°C). 4 ANDERSON (1972). 5 SUMINO *et al.* (1983). 6 CHANG and GRAHAM (1977). 7 SIMMONS and WANG (1971).

The entropy of melting at 1 atmosphere has been calculated for the range of molar volumes of liquid Fe_2SiO_4, and the results are compared to the calorimetric value obtained by STEBBINS and CARMICHAEL (1984). (Incidentally, it was discovered by trial and error that the model V^0 for FeO results in a molar volume for Fe_2SiO_4 which is most consistent with the calorimetric constraints if the 1400°C partial molar volume of liquid SiO_2 is 27.08 cm^3/gfw (Table 2; STEIN *et al.*, 1984), although the other values for SiO_2 result in a good approximation as well.) Using the STEIN *et al.* (1984) value for SiO_2 together with the range of raw values of V^0 and α for liquid FeO in Table 2, a range values for ΔS^0 are computed. These are shown in Figure AI-4. It can be seen that the model values of α and V^0 result in $\Delta S^0 = 60.73 \pm 1.84$ J/gfw · K, in excellent agreement with the calorimetrically determined value of 60.42 ± 0.74 J/gfw · K. All other volumes give rise to entropies which are seriously in conflict with the calorimetric data.

It is concluded that the partial molar volume and the thermal expansivity of liquid FeO are now well constrained. All experimental data which bear on liquid fayalite, these being the melting experiments at high pressure, the data on the forsterite–fayalite join, the calorimetric data and the volume correlations between Mg and Fe phases are internally consistent with the model α and V^0 parameters of liquid FeO listed in Table 2.

APPENDIX II

ANDERSON (1972) demonstrated that the law of corresponding states applies to crystalline metals. Much of the bulk modulus data which were reported were from the original measurements, and have been reexamined by other methods (*e.g.*, ultrasonic and Brillouin scattering). An updated data base has been compiled, together with bulk moduli for many metals in the liquid state at temperatures just above their melting points. These are listed in Table AII–1, portions of which have been shown above. The complete data base for metallic and nonmetallic elements is now plotted in Figure AII–1. There is no doubt that the bulk modulus of liquid metals varies systematically with specific volume, and this can be adequately described by the law of corresponding states.

Elastic data for crystalline binary compounds having cations in Groups IA and IIA are very well known. The compilations in ANDERSON (1972) have been updated and are listed in Table AII–2 and plotted in Figures 15, 16, and 17.