

## Implications of pressure-dependent compressibilities of silicate melts to calculated $P$ - $T$ origins of lavas

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### Abstract

Calculations of  $P$ - $T$  equilibration points of lavas with stipulated source mineralogies or megacrysts make use of integrals of the variation of activities of given oxide components in silicate melts with respect to pressure. Recent viscosity and density data suggest that the partial molar volume of  $\text{Al}_2\text{O}_3$  in a silicate melt ( $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$ ) is not linearly dependent on pressure, whereas the compressibility of pure  $\text{Al}_2\text{O}_3$  melt is more nearly a linear function of pressure. Consequently  $\Delta V(\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3 - \bar{V}^{\circ\text{melt}}/\text{Al}_2\text{O}_3)$  is pressure-dependent, and integration of the activity of  $\text{Al}_2\text{O}_3$  in the melt ( $a^{\text{melt}}/\text{Al}_2\text{O}_3$ ) is more complex than the equation given by Carmichael *et al.* (1977). Limited data on the  $\text{NaAlSi}_2\text{O}_6$  composition suggests that the maximum pressure-dependence of  $\Delta V$  at  $1350^\circ\text{C} = -9.92 \times 10^{-10}P^2 + 1.456 \times 10^{-5}P + 0.3291$  calbar $^{-1}$ , assuming that the non-linear portion of the density vs.  $P$  curve of  $\text{NaAlSi}_2\text{O}_6$  melt is predominantly due to the contraction of  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$  with pressure increase. Use of this equation for  $\Delta V$  will modify calculated  $P$ - $T$  equilibration points of lavas with stipulated solids. However, the equation for  $\Delta V$  must also be composition-dependent and should be regarded as strictly applicable to  $\text{NaAlSi}_2\text{O}_6$  melts alone. It is possible that the  $\Delta V$ 's of other components are also complex functions of pressure, so that uncertainty is attached to the routine integration of  $\Delta V$ 's with respect to pressure for equilibrium calculations without knowledge of their pressure-dependencies.

### Introduction and background

Recent papers by Kushiro and co-workers (Kushiro, 1976; Kushiro *et al.*, 1976; Fujii and Kushiro, 1977; Velde and Kushiro, 1978) on the viscosities and densities of silicate melts have suggested that the non-linear changes in these physical properties as a function of pressure in the range 0-25 kbar reflect changes in the coordination of Al in the melt. A similar conclusion was drawn by Mysen (1976) from a comparison of  $\text{CO}_2$  solubility data in albite melt as a function of pressure.

These results supported an earlier prediction by Waff (1975) concerning the probable pressure-dependence of Al coordination in silicate melts. Recently, Sharma *et al.* (1978) have suggested on the basis of a Raman spectroscopic study that Al does not undergo any coordination change from 4- to 6-fold as a result of increased pressure on a jadeite melt. This would imply a change in coordination of Al on melting of jadeite and a comparatively large entropy change of

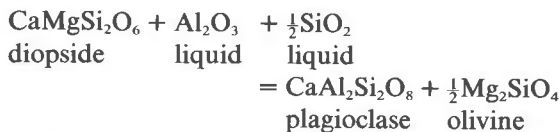
fusion ( $\Delta S_m$  and  $\Delta V_m$ ).  $\Delta S_m$  can be estimated as  $\approx 8.0$  cal $^\circ\text{K}^{-1}$  mole $^{-1}$  from  $\Delta H_m \approx 13$  kcal mole $^{-1}$  at 1630K (Bell and Davis, 1969) and  $(dT/dP)_m = 18^\circ\text{K}$  kbar $^{-1}$  (Williams and Kennedy, 1970).  $\Delta V_m \approx 6.02$  cc mole $^{-1}$ , and both values are of the same order as diopside [ $\Delta S_m = 11.11$  cal $^\circ\text{K}^{-1}$  mole $^{-1}$  and  $\Delta V_m = 6.14$  cc mole $^{-1}$  (Robie and Waldbaum, 1968)]. Coordination changes on melting have been observed in compounds such as the Cs halides (Johnson *et al.*, 1955), but are apparently not common in silicates. The interpretation of Sharma *et al.* (1978) is in conflict with the infrared and Al  $K\alpha$ -radiation data of Velde and Kushiro (1978) on the same composition. The precise details of the structure of Al-bearing silicate melts are currently in doubt; nevertheless, comparative studies of synthetic silicate melts demonstrate a more dramatic pressure effect on densities and viscosities for Al-bearing than for Al-free compositions (Kushiro, 1978).

A reasonable interpretation of all these data is that even if a coordination change of Al from 4- to 6-fold

in a silicate melt does not occur, there must be a non-linear change as a function of pressure in the geometry of the Al coordination polyhedra in particular, and consequently a non-linear change in the partial molar volume of  $\text{Al}_2\text{O}_3$  ( $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$ ) in silicate melts as a function of pressure. It is plausible that there are pressure-dependent, non-linear changes of the partial molar volumes of other oxide components of silicate melts.

There is as yet no evidence that the molar volume of pure  $\text{Al}_2\text{O}_3$  melt ( $\hat{V}^{\circ\text{melt}}/\text{Al}_2\text{O}_3$ ) is not linearly dependent on pressure. In addition, the coordination state of Al in corundum is 6-fold, and a similar coordination state is believed to exist in the pure melt (Waff, 1975). No possibility therefore exists of a coordination change of Al in pure  $\text{Al}_2\text{O}_3$  melt over the range 0–25 kbar. Any non-linearity of  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$  and hence  $\Delta V (= \bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3 - \hat{V}^{\circ\text{melt}}/\text{Al}_2\text{O}_3)$  as a function of pressure has important consequences for the calculation of equilibration  $P/T$ 's of lavas with specific upper mantle–crust sources according to the methods of Carmichael and co-workers (see Carmichael *et al.*, 1977 for a recent review).

In order that the significance of a pressure-dependent  $\Delta V$  be clear, some background to the employment of this parameter in calculated component activities at elevated pressures and temperatures will be given. A groundmass mineral assemblage can be used to define the activity of a given oxide in the silicate melt in question if the quenching temperature can be determined and this temperature be assumed to apply to the equilibration of all the groundmass phases. For example, the Fe–Ti oxides (ilmenite ss–magnetite ss) are most commonly used for determining the  $T$ - $f\text{O}_2$  of groundmass equilibration (see Carmichael *et al.*, p. 109–120, 1974, following Buddington and Lindsley, 1964). For defining the  $a^{\text{melt}}/\text{Al}_2\text{O}_3$  (activity of  $\text{Al}_2\text{O}_3$  in the melt), a groundmass assemblage of clinopyroxene, plagioclase, and olivine can be used, provided  $a^{\text{melt}}/\text{SiO}_2$  is known independently and given thermodynamic data for the phases involved in the equilibrium



Appropriate solution models for the crystalline phases have to be adopted. Knowledge of the variation with respect to pressure and temperature of  $a^{\text{melt}}/\text{Al}_2\text{O}_3$  is required in order to determine whether the

given lava was ever in equilibrium with a stipulated, parental source material. A component activity in the source material can be determined by analysis of an appropriate buffer reaction, and the pair of equations for the variation of  $a^{\text{melt}}/\text{Al}_2\text{O}_3$  with respect to  $P$  and  $T$  for source and lava can be solved. A line in  $P$ - $T$  space equivalent to  $a^{\text{melt}}/\text{Al}_2\text{O}_3 = a^{\text{source}}/\text{Al}_2\text{O}_3$  results. The intersection of two such lines for different components can be interpreted as the point in  $P$ - $T$  space where the lava might have been in equilibrium with the source material.

The temperature derivative of the  $a^{\text{melt}}/\text{Al}_2\text{O}_3$  (or any other oxide component) is currently assumed to be of the form expected in a regular solution, *i.e.*  $\ln a_i = \ln X_i + \phi/T$  where  $\phi$  is independent of  $T$  and a function of composition only (see Nicholls and Carmichael, 1972). The pressure derivative is given by

$$\left( \frac{\partial \ln a^{\text{melt}}/\text{Al}_2\text{O}_3}{\partial P} \right)_T = \frac{\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3 - \hat{V}^{\circ\text{melt}}/\text{Al}_2\text{O}_3}{RT} \quad (1)$$

The thermal expansion of pure oxide glasses is small, so  $\Delta V$  is taken to be independent of temperature. The critical step now follows in that  $\Delta V$  is assumed to be independent of pressure, so that upon integration (1) yields

$$\ln(a^{\text{melt}}/\text{Al}_2\text{O}_3)_T, P = \ln(a^{\text{melt}}/\text{Al}_2\text{O}_3)_T, \text{lbar} + \frac{\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3 - \hat{V}^{\circ\text{melt}}/\text{Al}_2\text{O}_3}{RT} (P - 1) \quad (2)$$

A non-linear change in  $\Delta V$  means that this in-

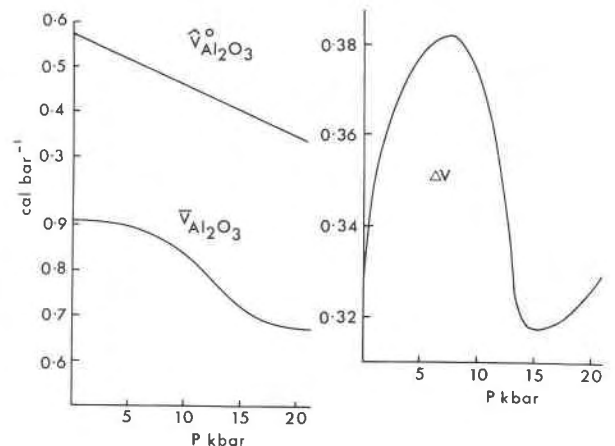


Fig. 1. The variation of  $\hat{V}^{\circ\text{melt}}/\text{Al}_2\text{O}_3$ ,  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$  and  $\Delta V$  for  $\text{NaAlSi}_2\text{O}_6$  composition as a function of pressure at  $1350^\circ\text{C}$ .

tegration is incomplete. It would be most useful therefore to determine the variation of  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$  with pressure so that appropriate integration of (1) can be attempted.

Kushiro (1976) presented data for the isothermal (1550°C) variation with pressure of the density of  $\text{NaAlSi}_2\text{O}_6$  glass. The observed non-linear increase in density of  $\text{NaAlSi}_2\text{O}_6$  glass over the pressure range 5–20 kbar was attributed by Kushiro to the gradual change of 4-fold coordinated Al to 6-fold coordination. The change in the melt was observed to be gradual compared with the equivalent sharp change in the solid reaction: albite = quartz + jadeite. Granted that the coordination changes may be incorrectly interpreted, comparative data show that Al-bearing silicate melts demonstrate the most dramatic changes in viscosity and density, so that the  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$ , compared with partial molar volumes of other components may be the most affected by pressure.

The problem of determining  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$  as a function of pressure is not easily solved, but can be attempted as follows by assuming that the excess increase in density of jadeite glass over the predicted compressibility is entirely due to a reduction in  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$ . This may well be an exaggeration, but will serve to demonstrate the possible consequences of a non-linear  $P$ -dependence of  $\Delta V$ . No claim is presented for great accuracy, but it is hoped that the method outlined will demonstrate the complexity that must be introduced into the integration of (1).

#### Calculation of $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$

Bottinga and Weill (1970) presented an empirical set of partial molar volumes for oxide components of silicate melts. They demonstrated that calculated densities of natural and synthetic silicate melts could be closely matched with experimentally-determined values through use of  $\bar{V}^{\text{melt}}/i$  data and the equation

$$\rho = \sum_i X_i \frac{M_i}{\bar{V}_i} \quad (3)$$

where  $X_i$ ,  $M_i$ , and  $\bar{V}_i$  represent the mole fraction, molecular weight, and partial molar volume of oxide component  $i$  respectively. At 1 bar, the calculated density of  $\text{NaAlSi}_2\text{O}_6$  melt at 1350°C is 2.328 gm  $\text{cc}^{-1}$ , whereas the density of the glass is quoted from other studies by Kushiro as 2.42 gm  $\text{cc}^{-1}$ . However, extrapolation of the  $\rho$ - $P$  plot to 1 bar gives a value of  $\approx 2.40$  gm  $\text{cc}^{-1}$ . For the following calculations, it is assumed that the density of the melt differs from that of the quenched glass by 0.072 gm  $\text{cc}^{-1}$ . This may not be

valid, as Fujii and Kushiro (1977) present evidence for a convergence with increased pressure of measured 1921 Kilauea tholeiite glass and melt densities. The compressibility ( $\beta$ ) of  $\text{NaAlSi}_2\text{O}_6$  melt is taken from an extrapolation of the linear portions of the  $\rho$ - $P$  plot presented by Kushiro (1976). Given the calculated 1 bar  $\rho$  and  $\beta$  for  $\text{NaAlSi}_2\text{O}_6$  melt, it is possible to calculate the  $\rho$ 's at higher pressures. The appropriate predicted and actual values for glass and melt are given in Table 1.

Given the actual melt densities, it is possible to determine  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$  through substitution of (3) with actual melt densities, after allowance for overall contractions of  $\bar{V}_i$  with pressure by substitution of the same equation with the predicted melt densities. The increase in melt density over that predicted is here supposed to result solely from the contraction of  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$ . The calculated  $\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$  at the different pressures is given in Table 1 and implies a  $\approx 26$  percent decrease in molar volume at 21 kbar in comparison with the 1 bar value.

Carmichael *et al.* (1977) give the  $P$  and  $T$  dependence of  $\hat{V}^{\circ \text{melt}}/\text{Al}_2\text{O}_3$  (calbar $^{-1}$ ) as ( $T$  in K):

$$\hat{V}^{\circ \text{melt}}/\text{Al}_2\text{O}_3 = 330.99 \times 10^{-6}T + 0.03986 - 11.78 \times 10^{-6}P \quad (4)$$

and point out that considerable uncertainty is attached to the compressibility term. In fact, the isothermal (1350°C) decrease in  $\hat{V}^{\circ \text{melt}}/\text{Al}_2\text{O}_3$  with increased pressure would result in practically zero  $\hat{V}^{\circ \text{melt}}/\text{Al}_2\text{O}_3$  at approximately 45 kbar, so the compressibility seems to be too large. However, the value as given will be adopted for the present and the  $\Delta V$ 's (calbar $^{-1}$ ) are given in Table 2 for  $\bar{V}^{\text{jadeite melt}}/\text{Al}_2\text{O}_3 - \hat{V}^{\circ \text{melt}}/\text{Al}_2\text{O}_3$  over the pressure range 1 bar to 21 kbar

Table 1. Comparison of predicted and actual  $\text{NaAlSi}_2\text{O}_6$  glass and melt densities

	glass		melt		$\bar{V}^{\text{melt}}/\text{Al}_2\text{O}_3$
	predicted	actual*	predicted	actual*	
1 bar	2.40	2.40	2.328	2.328	37.91 cc mole $^{-1}$
5 kbar	2.415	2.418	2.343	2.346	37.454
10 kbar	2.435	2.469	2.363	2.397	34.93
15 kbar	2.445	2.549	2.373	2.477	30.04
21 kbar	2.450	2.584	2.378	2.512	28.05

\*data from Kushiro (1976) for glass and calculated assuming  $\Delta\rho = 0.072$  gm  $\text{cc}^{-1}$  for melt,  $\beta = -3 \times 10^{-6}$  calbar $^{-2}$ .

Table 2. Variation of  $\Delta V$  with pressure at 1350°C

	$\bar{v}_{\text{jadeite melt}/\text{Al}_2\text{O}_3}$	$\hat{v}^0_{\text{melt}/\text{Al}_2\text{O}_3}$	$\Delta V$
1 bar	0.9061	0.577	0.3291
5 kbar	0.8951	0.577	0.3771
10 kbar	0.8348	0.4593	0.3755
15 kbar	0.7180	0.4004	0.3176
21 kbar	0.6704	0.3414	0.3290

Graphical display of these values is given in Figure 1.

at 1350°C. At pressures up to 15 kbar, the variation of  $\Delta V$  with  $P$  can be given as ( $P$  in bars):

$$\Delta V = -9.92 \times 10^{-10} P^2 + 1.456 \times 10^{-5} P + 0.3291 \quad (5)$$

Substitution of equation (1) with (5) and integration gives

$$\ln(a^{\text{melt}}/\text{Al}_2\text{O}_3)T, P = \ln(a^{\text{melt}}/\text{Al}_2\text{O}_3), T, 1\text{bar} \\ + (-3.307 \times 10^{-10} P^3 + 7.28 \times 10^{-6} P^2 \\ + 0.3291P - 0.32911)/RT$$

Lack of data prevents application of this equation to pressures greater than 15–20 kbar.

### Comparison of calculated $a^{\text{melt}}/\text{Al}_2\text{O}_3$

As an example of the effect on calculated  $a^{\text{melt}}/\text{Al}_2\text{O}_3$  through employment of equation (5) rather than (2), the example given by Carmichael *et al.* (1974, p. 117) will be studied. Taking the compositional data for a basalt and lherzolite xenoliths, Carmichael *et al.* calculate an equilibration  $T$  and  $P$  of 1173°C, 19.9 kbar. Substitution of their appropriate equation (3–61) gives  $\log(a^{\text{melt}}/\text{Al}_2\text{O}_3)_{1173,19.9}$  as  $-2.755$ .

Assuming the same regular solution model and substituting the pressure derivative as given in (5) (ignoring the  $P$  range restriction) results in  $\log(a^{\text{melt}}/\text{Al}_2\text{O}_3)_{1173,19.9} = -2.876$ .

In general, (5) gives lower activities at  $P$  and  $T$  than does the analogous Carmichael *et al.* (1974) equation.

Unfortunately, the form of equation (5) prevents the simultaneous solution of  $P$ - $T$  equilibration given equations for 2 component activities. It should further be realized that (a) the constants given in (5) are

derived from an analysis of  $\text{NaAlSi}_2\text{O}_6$  melt behavior only, and thus a compositional dependence must be introduced if further refinement be attempted of the computation of the pressure derivative of  $a^{\text{melt}}/\text{Al}_2\text{O}_3$ ; and (b) there is a possibility that the emphasis in this discussion on  $\text{Al}_2\text{O}_3$  is exaggerated and that there are similar, if comparatively muted, pressure-dependent non-linearities in the  $\bar{V}$ 's of other oxide components.

In conclusion, there must be considerable doubt as to the validity of ignoring the pressure-dependence of  $\Delta V$  in determining  $P$ - $T$  equilibration values for lavas. Further analysis will require detailed knowledge of  $\bar{V}_1$  as a function both of pressure and composition before acceptance of calculated  $P/T$  points may be permitted.

### Acknowledgments

Discussions with I. Kushiro and I. Jackson were of constructive help.

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*Manuscript received, June 19, 1978.*

*accepted for publication, March 6, 1979.*