

## LETTERS

### Extrapolated partial molar densities of SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, and other oxides in silicate melts

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#### ABSTRACT

Partial molar densities of oxides in natural silicate melts can be estimated to useful precision by exploiting their strong correlation with densities of the corresponding solid oxides, reflecting the close structural similarity between silicate solids and silicate melts. Using this extrapolation method, partial molar density (in grams per mole-cubic centimeter at 1400 °C) is inferred to be 2.0 for SO<sub>3</sub> and 2.3 for P<sub>2</sub>O<sub>5</sub>; i.e., the partial molar volumes,  $V_{i,m}$  (in cubic centimeters per mole), are 40 and 61, respectively. The inferred  $dV_{i,m}/dT$  (in cubic centimeters per mole-kelvin) are 0.0056 for SO<sub>3</sub> and 0.0085 for P<sub>2</sub>O<sub>5</sub>. Analogous estimates are also given for V<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, and Nd<sub>2</sub>O<sub>3</sub>. The inferred uncertainty for the  $V_{i,m}$  estimates is 12% (1 $\sigma$ , relative), although the  $V_{i,m}$  for Cr<sub>2</sub>O<sub>3</sub> is somewhat more uncertain because on melting, this oxide probably changes from octahedral to largely tetrahedral coordination.

#### INTRODUCTION

The densities of natural silicate melts are diverse, with important ramifications for the motion of crystals in magmatic suspensions and the movement of magma vis-à-vis surrounding rock. Conveniently, the molar volume of low-pressure natural silicate liquid is a nearly linear function of composition and temperature, so that for any given  $T$ , the density of a melt can be estimated to good precision by simply summing the partial molar volumes ( $V_{i,m}$ ) of its oxide components (Bottinga and Weill, 1970). Experimental data constrain the  $V_{i,m}$  to within about 1% (relative) for the ten or so most naturally abundant oxides (Lange and Carmichael, 1987). However, constraints for volatiles such as H<sub>2</sub>O and CO<sub>2</sub> are far less precise, and according to a recent review (Lange, 1994), no measurements exist regarding the effect of SO<sub>3</sub> on melt density. Other potentially significant oxides for which experimental constraints are lacking include Cr<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and rare earth element (REE) oxides. In addition, available experimental data appear inadequate for determining the complex effects of P<sub>2</sub>O<sub>5</sub> (Dingwell et al., 1992; Toplis et al., 1994).

Recently, Marc Norman admonished that I should consider the potential influence of an anticipated heavy proportion of dissolved SO<sub>3</sub> on the density of a magma that I asserted would be strongly buoyant relative to surrounding crustal rocks. Lange's (1994) excellent review on the effects of volatiles on melt density initially led me to fear that the effect of SO<sub>3</sub> could not be determined. However, on further study I found that the effect of any oxide on melt density can be estimated to useful precision by exploiting a strong correlation between the density of solid oxides and the partial molar density of oxides in silicate melts.

#### RESULTS

Figure 1 shows the relationship between solid density,  $\rho_s$ , at  $-73$  °C and partial molar density,  $\rho_{i,m}$ , in silicate melt at 1400 °C. The reason for adopting  $-73$  °C (200 K) as the reference  $T$  is that solid CO<sub>2</sub> is unstable at  $T$  higher than  $-79$  °C. Data for  $\rho_s$  were taken mainly from the *CRC Handbook of Chemistry and Physics* (Lide, 1991–92) and Roberts et al. (1974), with slight adjustments ( $\times 1.0025$ ) for contraction between 0 and  $-73$  °C. In cases in which more than one mineral appears stable (e.g., for TiO<sub>2</sub>, brookite, octahedrite, and rutile each might be stable; for Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and corundum each might be stable), the average density was used. Data for  $\rho_{i,m}$  were taken mainly from Lange and Carmichael (1987) and Bottinga et al. (1983). Contrasting results for the  $\rho_{i,m}$  of P<sub>2</sub>O<sub>5</sub> in haplogranitic and ferrobaltic melts (Dingwell et al., 1992; Toplis et al., 1994) were not used in the database for regression. A result for the  $\rho_{i,m}$  of B<sub>2</sub>O<sub>3</sub> in 750 °C haplogranitic melt (Dingwell et al., 1992) was likewise omitted from the regression because extrapolation from such an extreme composition and  $T$  seems unwarranted (both B<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> are further discussed below).

The remaining 20 oxides for which experimental data are available yield a linear regression correlation coefficient of 0.97 and a log regression correlation coefficient of 0.98. In Figure 1, the heavy curve represents the fit based on log regression,  $\rho_{i,m} = 0.9789\rho_s^{1.0329}$ , but to facilitate interpolation (and to document the comparable strength of the linear correlation) the  $x$  and  $y$  scales are linear.

For thermodynamical convenience, the literature customarily discusses the problem of silicate melt density exclusively in terms of partial molar volume,  $V_{i,m}$ , instead of partial molar density,  $\rho_{i,m}$ . These two parameters are

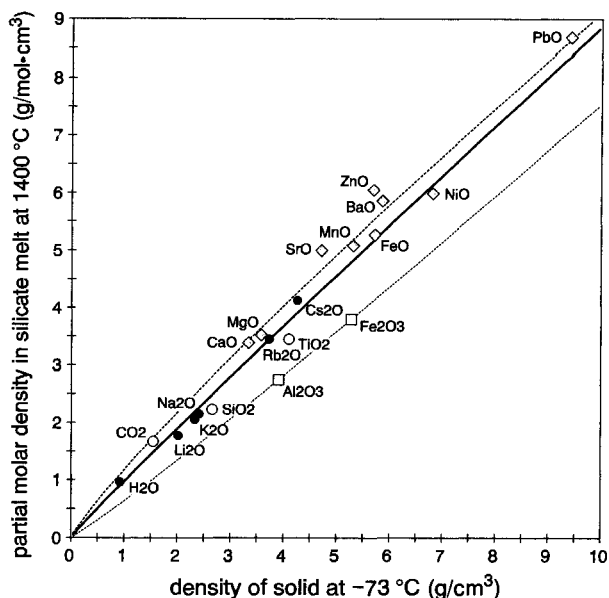


Fig. 1. Solid oxide density at  $-73\text{ }^{\circ}\text{C}$  (200 K) vs. partial molar density in  $1400\text{ }^{\circ}\text{C}$  silicate melts. The heavy curve is a log regression fit to all plotted data. Dotted curves are log regression fits to subsets of the total database, restricted in one case to diatomic oxides (gray diamonds) and in the other to  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  (gray squares). Other symbols represent dioxides (open circles) and alkali oxides +  $\text{H}_2\text{O}$  (solid circles).

not simply reciprocals because the molecular weights of the oxides of interest range from 18 ( $\text{H}_2\text{O}$ ) to 336 ( $\text{Nd}_2\text{O}_3$ ). Of the 20 oxides in the database, the one with the lowest  $1400\text{ }^{\circ}\text{C}$   $V_{i,m}$  ( $\text{MgO}$ ) ranks tenth in terms of  $\rho_{i,m}$ ; the one with the highest  $1400\text{ }^{\circ}\text{C}$   $\rho_{i,m}$  ( $\text{PbO}$ ) ranks eleventh in terms of  $V_{i,m}$ . Thus, a regression of solid molar volume,  $V_s$ , against  $V_{i,m}$  (Fig. 2, the heavy curve:  $V_{i,m} = 1.1074 V_s^{0.99266}$ ) constrains the overall density and volume problem in a slightly different way than the  $\rho_s$  vs.  $\rho_{i,m}$  regression. Of course, to the extent that the correlation is

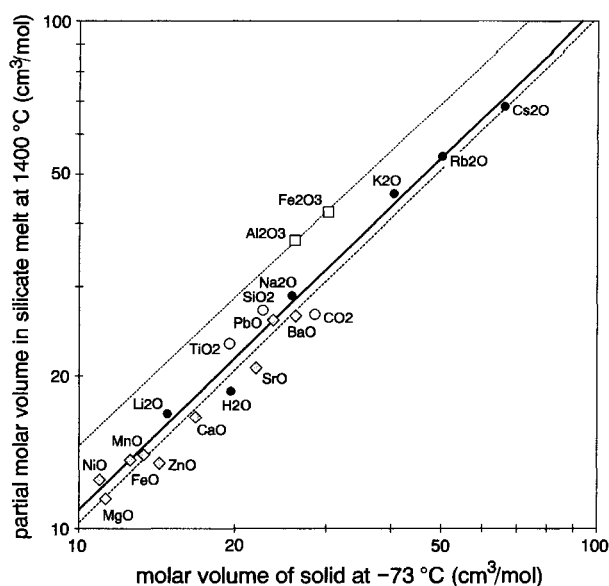


Fig. 2. Solid oxide molar volume at  $-73\text{ }^{\circ}\text{C}$  (200 K) vs. partial molar volume in  $1400\text{ }^{\circ}\text{C}$  silicate melts. The three curves are analogous to those in Fig. 1 (including forcing of the regressions to pass through  $V_s$  and  $V_{i,m}$  both equal to infinity, i.e.,  $\rho_s$  and  $\rho_{i,m}$  both equal to zero).

not a statistical fluke, it should appear comparably strong in both Figures 1 and 2 and should lead to similar predictions for any given  $V_{i,m}$  (or  $\rho_{i,m}$ ) as a function of  $V_s$  (or  $\rho_s$ ). Several such predictions are shown in Table 1, where the two regressions indeed show good agreement.

A better way to gauge the precision of these estimates for  $V_{i,m}$  is to compare the 20 known values with the values implied by the regressions. If  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  (discussed below) are excluded from this comparison, one standard deviation for the predicted/known ratio is 8% (relative); including  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , one standard deviation is 12%. Although 12%  $1\sigma$  uncertainty is at least an order of mag-

TABLE 1. Estimated partial molar volumes and thermal expansivities of oxide components

Oxide	Solid density, $\rho_s$ ( $\text{g}/\text{cm}^3$ at $-73\text{ }^{\circ}\text{C}$ )	Partial molar volume, $V_{i,m}$ , in $1400\text{ }^{\circ}\text{C}$ melts ( $\text{cm}^3/\text{mol}$ )		Partial molar density, $\rho_{i,m}$ [ $\text{g}/(\text{mol}\cdot\text{cm}^3)$ at $1400\text{ }^{\circ}\text{C}$ ]	$dV_{i,m}/dT$ [ $\text{cm}^3/(\text{mol}\cdot\text{K}) \times 10^3$ ]
		From $V_s$ - $V_{i,m}$ regression	From $\rho_s$ - $\rho_{i,m}$ regression		
$\text{P}_2\text{O}_5^*$	2.5	60.9	60.4	2.34	8.5
$\text{SO}_3$	2.14	40.4	39.8	2.00	5.6
$\text{V}_2\text{O}_5$	3.36	58.2	58.5	3.12	8.2
$\text{Cr}_2\text{O}_3^{**}$	5.22	31.4	32.0	4.8	4.4
Alternative model**		40.8	40.5	3.74	5.7
$\text{Y}_2\text{O}_3$	4.96	49.0	49.9	4.57	6.9
$\text{ZrO}_2$	5.81	22.9	23.4	5.3	3.2
$\text{La}_2\text{O}_3$	6.53	53.7	55.3	6.0	7.6
$\text{Nd}_2\text{O}_3$	7.26	49.9	51.6	6.6	7.1
$\text{Ce}_2\text{O}_3$	6.88	51.4	53.0	6.3	7.3

Note: Results for  $\rho_{i,m}$  are based on averages of two results shown for  $V_{i,m}$ .

\* Results for  $\text{P}_2\text{O}_5$  may be compared with a  $V_{i,m}$  measurement for ferrobasic melt at  $1300\text{ }^{\circ}\text{C}$  (Toplis et al., 1994):  $64.5\text{ cm}^3/\text{mol}$ , which extrapolates to  $65.4\text{ cm}^3/\text{mol}$  at  $1400\text{ }^{\circ}\text{C}$ . Toplis et al. (1994) cautioned that the role of  $\text{P}_2\text{O}_5$  in silicate melts is complex, and thus their result should not be extrapolated far from the compositional range of ferrobasic melt (for further discussion, see text).

\*\* Tabulated estimates generally assume oxide features the same coordination in melt as in solid, but because  $\text{Cr}_2\text{O}_3$  possibly occurs largely in low- $\rho$  tetrahedral coordination in silicate melts, an alternative model, based on fits to  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  alone, is also listed for this oxide (see text).

nitide worse than the precision estimates given for ten oxides by Lange and Carmichael (1987), this approach still provides useful constraints because the known  $\rho_{i,m}$  and  $V_{i,m}$  (Figs. 1 and 2) range over factors of many hundreds of percent.

Thermal expansivity can be modeled in terms of a coefficient of thermal expansion,  $\alpha_i$ , defined by

$$\alpha_i = \frac{(V_{i,T1} - V_{i,T2})/(T1 - T2)}{V_{i,T1}}$$

where, to span the  $T$  range of most magmas,  $T1 = 1400$  °C and  $T2 = 800$  °C. The average  $\alpha_i$  for 18 oxides (Bottinga et al., 1983; Lange and Carmichael, 1987) is  $2.7 \times 10^{-4} \text{ K}^{-1}$ . However, the alkali oxides ( $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ , and  $\text{Cs}_2\text{O}$ ) have extraordinarily high  $\alpha_i$ , which is probably a result of their low cation field strengths ( $0.11$ – $0.23 \text{ e}/\text{\AA}^2$ ; Lange and Carmichael, 1990). All the oxides listed in Table 1 have moderate to high cation field strengths [none lower than  $0.50 \text{ e}/\text{\AA}^2$  ( $\text{La}_2\text{O}_3$ )]. With the five alkali oxides excluded from the database, the average  $\alpha_i$  is  $1.68 \times 10^{-4} \text{ K}^{-1}$ . As another approach to estimating  $\alpha_i$ , the same regression technique used in Figures 1 and 2 can be applied for 800 °C. This approach implies that for the oxides listed in Table 1,  $\alpha_i$  ranges from  $0.9 \times 10^{-4}$  ( $\text{SO}_3$  and  $\text{P}_2\text{O}_5$ ) to  $1.3 \times 10^{-4}$  ( $\text{Nd}_2\text{O}_3$ ) and averages  $1.13 \times 10^{-4} \text{ K}^{-1}$ . These extrapolations are far too imprecise (largely because of uncertainties in  $\alpha_i$  for the known oxides) for the range ( $0.9$ – $1.3 \times 10^{-4} \text{ K}^{-1}$ ) to be considered significant. The best way to estimate  $\alpha_i$  is probably to apply the average of  $1.68 \times 10^{-4}$  and  $1.13 \times 10^{-4}$  (i.e.,  $1.4 \times 10^{-4} \text{ K}^{-1}$ ) to all the oxides in Table 1. The table includes  $dV_{i,m}/dT$  estimates derived by this method.

## DISCUSSION

For most oxides, the relationship between  $\rho_{i,m}$  and  $\rho_s$  is remarkably simple. At 1400 °C, the simple equation  $\rho_{i,m} = 0.924\rho_s$  fits the data of Figure 1 virtually as well as the log regression employed for Table 1 (and  $V_{i,m} = 1.08V_s$  fits the data of Fig. 2 about equally well). At 800 °C, the equation  $\rho_{i,m} = 0.99\rho_s$  (and  $V_{i,m} = 1.01V_s$ ) fits nearly as well as more complex models. This simple relationship reflects the high degree of structural similarity between silicate solids and silicate melts (Hess, 1991).

The two major exceptions, which show relatively large expansion on melting, are  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . These two oxides are unusual because their coordination shifts from octahedral in solids to largely tetrahedral in melts (Bottinga et al., 1983; Lange and Carmichael, 1990). Separate regressions are shown for this pair of oxides in Figures 1 and 2 to emphasize the pair's deviation from the overall trend.  $\text{Cr}_2\text{O}_3$ , in which  $\text{Cr}^{3+}$  has an intermediate radius and the same valence as  $\text{Al}^{3+}$  in  $\text{Al}_2\text{O}_3$  and  $\text{Fe}^{3+}$  in  $\text{Fe}_2\text{O}_3$ , possibly shifts likewise to partly tetrahedral coordination in melts. However, Faure (1991) listed only octahedral coordination for  $\text{Cr}^{3+}$ , although he listed tetrahedral coordination for  $\text{Cr}^{4+}$  and  $\text{Cr}^{6+}$ . For  $\text{Cr}_2\text{O}_3$ , Table 1 includes results based on fits to only  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . I

recommend that these higher  $V_{i,m}$  results be averaged with the regular results for this oxide.

For another sesquioxide,  $\text{B}_2\text{O}_3$ , the only experimental result is for haplogranitic melt at 750 °C (Dingwell et al., 1992). A shift in B coordination from triangular in solid  $\text{B}_2\text{O}_3$  (Prewitt and Shannon, 1968) to largely tetrahedral in silicate melts is probably most extensive if the melt  $\text{SiO}_2$  content is high (Hess, 1991). Thus, the Dingwell et al. (1992) result may not be generally representative for the  $V_{i,m}$  of  $\text{B}_2\text{O}_3$  in silicate melts. It is interesting to note, however, that the Dingwell et al. (1992)  $V_{i,m}$  for  $\text{B}_2\text{O}_3$  is modeled far better on the basis of a regression using only  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  (the model result, averaging the  $\rho_{i,m}$  and  $V_{i,m}$  regressions, is 1.01 times the measured value) than the normal, indiscriminating regression method (model result is 1.45 times the measured value). Apparently, at least in haplogranitic systems (in which the coordination shift may be especially strong),  $\text{B}_2\text{O}_3$  exhibits expansion on melting similar to  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ .

Separate regressions are also shown in Figures 1 and 2 for the diatomic oxides, which give some indication of distributing along a trend significantly to the high- $\rho$  side of the overall trend. Besides the oxides listed in Table 1, the reader can easily find the  $\rho_s$  for any other oxide of interest and use Figures 1 and 2 to interpolate the corresponding  $\rho_{i,m}$  (or  $V_{i,m}$ ).

Toplis et al. (1994) noted that their result for the  $V_{i,m}$  of  $\text{P}_2\text{O}_5$  in 1300 °C ferrobaltic melt is much lower than a simple extrapolation from the result of Dingwell et al. (1992) for a 750 °C haplogranitic melt would suggest. Toplis et al. (1994) interpreted this contrast as a consequence of the sensitivity of  $\text{P}_2\text{O}_5$  behavior in silicate melt to the detailed composition, especially the  $\text{Fe}^{3+}$  content, of the melt. Despite this complexity, and an uncommonly high uncertainty regarding the  $\rho_s$  for  $\text{P}_2\text{O}_5$ , the extrapolation method (Table 1) shows fairly good agreement with the Toplis et al. (1994) result for 1300 °C ferrobaltic melt. In any case, it seems clear that a high content of  $\text{P}_2\text{O}_5$  in a natural silicate melt tends to impart a low density.

As reviewed by Lange (1994), current experimental constraints also leave great uncertainty regarding the  $V_{i,m}$  for  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Results from the extrapolation method (Figs. 1 and 2) tend to confirm the values recommended by Lange (1994) for the  $V_{i,m}$  of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

At present, no experimental constraints exist for the  $V_{i,m}$  of  $\text{SO}_3$  in silicate melts (Lange, 1994). The speciation of dissolved S in silicate melts is a strong function of  $f_{\text{O}_2}$ . If  $f_{\text{O}_2}$  is greater than roughly 1.5 log 10 (bar) units above the FMQ buffer, S dissolves mainly as  $\text{SO}_4^{2-}$  (Carroll and Webster, 1994); at lower  $f_{\text{O}_2}$  it dissolves mainly as  $\text{S}^{2-}$ . Dissolution of S as an ionic oxide might lead to some deviation from the general oxide trend of Figures 1 and 2. However, in the case of C, which dissolves as either molecular  $\text{CO}_2$  or as  $\text{CO}_3^{2-}$ , depending mainly on the activity of silica (Fine and Stolper, 1985), the speciation has no significant effect on the  $V_{i,m}$  for total dissolved  $\text{CO}_2$  (Lange, 1994). Assuming that the  $V_{i,m}$  of  $\text{SO}_3$

is not greatly affected by ionization to  $\text{SO}_3^{2-}$ , Table 1 implies that the  $\rho_{i,m}$  of  $\text{SO}_3$  is probably lower (and certainly is not significantly higher) than the density of even the dacitic types of magma for which the highest  $\text{SO}_3$  contents (up to roughly 3 wt%: Carroll and Webster, 1994) have been inferred.

Basic properties of silicate melts, and even solid silicates, might be elucidated by acquiring  $\rho_{i,m}$  data for additional oxides, even naturally scarce ones such as  $\text{GeO}_2$  and  $\text{HfO}_4$ , for purposes of comparison vs. the correlation (or perhaps separate correlations, for varying structural types of oxide molecules) manifested in Figures 1 and 2. It would also be interesting to ascertain the degree to which elements dissolved as reduced species (e.g.,  $\text{S}^{2-}$ ; the  $\rho_s$  of S is  $2.0 \text{ g/cm}^3$ ) distribute along a similar trend.

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