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PARTIAL MOLAR VOLUMES OF OXIDE COMPONENTS IN SILICATE LIQUIDS

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ABSTRACT

Densities of 21 silicate liquids have been determined from 1000° to 1600°C. The compositions studied contain from two to eight oxide components and have the following ranges in composition (mole %): SiO_2, 35-79%; TiO_2, 4-36%; Al_2O_3, 5-25%; FeO, 11-41%; MgO, 7-28%; CaO, 7-35%; Na_2O, 5-50%; and K_2O, 4-20%. The compositions thus cover the upper range observed in magmas for each oxide. Precision for each determination of liquid density is always better than ±1%.

Volumes/gfw (gram formula weight) calculated from the density measurements and the chemical compositions of the analyzed liquids have been combined with data on 96 silicate liquids reported in the literature. From this data set we derive, by using multiple linear regression, partial molar volumes of the components SiO_2, TiO_2, Al_2O_3, FeO, MgO, CaO, Na_2O, and K_2O at five temperatures. The standard deviation of the multiple regression is 1.8% of the molar volumes, which is considered about equal to the total errors due to compositional and instrumental uncertainties.

These derived partial molar volumes have been used to calculate

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volumes/gfw of natural silicate liquid which are found to agree within 1% of the measured values. No compositional dependence of the partial molar volumes can be detected within the error considered to be typical of the measurements. This is further supported by the close agreement between the calculated volumes of $CaMgSi_2O_6$ and Fe_2SiO_4 liquids derived from the initial slopes of their fusion curves and their heats of fusion, and the volumes obtained by summing the respective partial molar volumes. The experimental data indicate that silicate liquids mix ideally with respect to volume, over the temperature and composition range of this data set.

INTRODUCTION

Although silicate liquids are the primary constituents of magmas, few systematic attempts have been made to determine their chemical and physical properties. The present study is part of an effort to fill the gaps in knowledge of silicate liquid properties. Densities of 21 silicate liquids have been determined as a function of temperature. This report discusses the method and apparatus used in these determinations, presents the results of the experiments and derives a consistent set of relationships involving the compositional and temperature dependence of density and volume in silicate melts.

Bottinga and Weill (1970) have summarized the existing work on silicate liquid density determinations. From these data, those authors obtained a set of partial molar volumes of oxide components in silicate melts which enable one to calculate the density or volume of any multi-component silicate liquid within the compositional and temperature range of the experiments at 1 bar. Most of the existing volume data involve systems with two or three oxide components (see Bottinga and Weill, 1970, for a summary of these data) and none of the liquids contained TiO_2 as a component. The present experiments were designed to test the results of Bottinga and Weill (1970) and to add to the data set systems of more than three components and also liquids containing TiO_2 as a component.

EXPERIMENTAL APPARATUS

The apparatus used for the density determination is similar to that described by Bockris et al. (1956). It consists of a platinum/rhodium wound resistance furnace and temperature controller that operates

in the range of 500° to 1600°C. The furnace is mounted on a hydraulic jack so that it can be raised and lowered, with the distance measured on a micrometer dial gauge. A concrete platform mounted above the furnace supports an electronic balance that has a precision of ±0.001 g. The silicate liquid sample, in a platinum or iron crucible, is placed in the furnace whose temperature is measured with a Pt/Pt10%Rh thermocouple calibrated periodically at the melting point of gold. A platinum bob, the volume of which is known at room temperature, is suspended from the balance in the furnace atmosphere. The furnace and crucible containing the silicate liquid are raised until the tip of the bob makes contact with the surface of the liquid. The contact causes a deflection on the balance, and the point at which this occurs is noted on the micrometer gauge. Then the crucible and liquid are raised a constant distance (2.5 or 2.0 cm) to submerge the Pt bob, and the weight of the bob is read on the balance.

The buoyancy of the bob (weight in air less weight in liquid) can then be used to calculate the density from the formula of Archimedes:

$$\rho = (B + S)/V(T) \qquad (1)$$

where B = buoyancy of the bob uncorrected for surface tension,

ρ = density of the liquid,

S = correction for surface tension on the emergent stem of the Pt bob,

$V(T)$ = the known submerged volume of the bob at the temperature (K) of measurement.

In this case $V(T) = V_{290K}\,[\exp(-4.605 \times 10^{-3} + 1.293 \times 10^{-5}T + 1.0269 \times 10^{-8}T^2 - 3.2335 \times 10^{-13}T^3)]$

where the thermal expansion of pure Pt is taken from Waseda et al. (1975) and Edwards et al. (1951), and V_{290K} is the volume of the submerged Pt bob measured at 290 K by weighing in air and correcting to vacuum and subtracting the volume of the non-submerged stem of the bob.

The effect of surface tension on the emergent stem of the bob was eliminated by making runs on each liquid composition using two bobs with different volumes but with the same stem diameter. Density was then determined by first fitting a least squares line to the buoyancy-temperature data on the large bob and then solving for density at the measured temperature of the small bob. The procedure was then inverted, first fitting a least squares line to the small bob buoyancy as a function of temperature and then solving for density at the measured temperature of the large bob.

For compositions containing FeO as a component, pure Fe crucibles were used to contain the liquid. N_2 or Ar gas was then passed through the furnace tube four or five times per hour. Thus the oxygen fugacity, although not known, would have been buffered by the oxygen content of the gas and the Fe crucible.

Because a plot of buoyancy-temperature should be linear (Bockris et al., 1956), the effect of bubbles in the liquid or adhering to the Pt bob could be detected by deviations from linearity. A drastic change in oxidation state of Fe in the Fe-bearing compositions or a loss of FeO from the liquid should also show a deviation from linearity. Thus, compositions were run until a straight line relationship between buoyancy and temperature was reasonably assured.

SAMPLE PREPARATION

Reagent grade SiO_2, TiO_2, Al_2O_3, Fe, Fe_2O_3, MgO, $CaCO_3$, Na_2CO_3, K_2CO_3, and $Na_2SiO_3.9H_2O$ powders were used for preparation of the liquids. The powders were weighed in the proportions required and then mixed in glass jars. For all synthetic compositions, except those containing Fe, the mixed powders were then fused in a large Pt crucible at 1500° - 1700^oC in a glass-making furnace. The liquids were then checked for bubbles periodically, and when a bubble-free liquid was obtained, it was poured into a graphite mold and quenched to a glass. The glass block was then broken into large chunks that were placed in the smaller Pt crucibles and heated in the furnace until all bubbles were again exsolved. After determining the density of each liquid by the method described above, the liquids were poured onto a graphite slab, quenched, crushed, and analyzed by the method of Carmichael (1970).

For compositions containing FeO, the procedure was somewhat different. The mixed powders were placed directly into the Fe crucibles and heated in a vacuum furnace for up to 12 hours at temperatures of 1300° - 1400^oC. After cooling under vacuum, the resulting glasses were placed directly in the experimental furnace in the presence of N_2 or Ar gas and density was measured as described above. The liquids were then cooled in the furnace in the presence of the gas, cored out of the crucibles, and analyzed. A sample of a Kilauea lava was crushed to powder, placed in the Fe crucible and run after the bubbles had been removed at 1300° - 1400^oC.

The analyses of the investigated liquids are presented in Table I.

They include 2 two-component systems, 8 three-component systems, 6 four-component systems, 3 five-component systems, and 1 seven-component system, as well as the natural composition containing all of the oxides. The choice of compositions was limited by two factors: first, the liquidus temperatures were required to fall within the controlled temperature range of the furnace, and second, the viscosity of the liquids had to be low enough that bubbles could successfully be removed and the Pt bob could settle to its required depth within a reasonable amount of time.

RESULTS

Equations of specific volume as a function of temperature for each of the compositions studied are presented in Table II. These equations were obtained by fitting a straight line through the two sets of density data obtained from each of the two bobs. Three examples of the data used to fit the density-temperature equations are shown in Figure 1, where a worst case, intermediate case, and best case are shown. The most scattered results were obtained on compositions 2 and 15, the most viscous liquids studied. Nevertheless, the maximum deviation from the least squares line for composition 2 is within 0.85%, indicating that the precision for all of the determinations is well within ±1%. Attributing reasonable uncertainties to the various parameters in Equation 1, an uncertainty can be obtained for the density of any composition due to instrumental error. For example, if for the sodium silicate liquid (NS) at a temperature of 1370 K, the buoyancy measured with the large bob is 2.766 ± 0.002 g, that with the small bob is 1.420 ± 0.002 g and as the respective volumes of the bobs (at

1370 k) are 1.2445 ± 0.001 cm^3 and 0.6610 ± 0.001 cm^3, then the density is 2.307 with an uncertainty of ± 0.0074 or ± 0.3%. Thus the uncertainties in the measured density or specific volume due to propagation of errors are within the limits of reproducibility.

PARTIAL MOLAR VOLUMES

The partial molar volume of any component i in a solution is defined as:

$$\bar{v}_i = (\partial V/\partial n_i)_{P,T,n_j}$$

where V is the total volume of the system,

and n is the number of moles of the component i or the components j which do not include i.

In practice, partial molar volumes are difficult to determine, especially in systems containing as many as eight components. The most systematic method of determining any compositional dependence of the partial molar volumes would be to use the method of Darken (1950) amd make measurements along pseudo-binary joins where the ratios of all other components except those involving the component of interest are held constant. This approach, however, is limited by the fact that in order to measure enough pseudo-binaries to completely describe an eight-component system, an inordinate number of experiments are required. Furthermore, compositions near end member oxides are often not accessible to experimental investigation due to their high melting temperatures or to their thermal decomposition.

Riebling's (1966) study of the system Na_2O - Al_2O_3 - SiO_2 offers a view of a three-component system in terms of several pseudo-binaries. His raw data along the pseudo-binary SiO_2 - (0.5 Na_2O_3, 0.5 Al_2O_3) shows an apparent compositional dependence for $\bar{v}_{SiO_2}$ and $v_{NaAlSi_3O_8}$. However, within his quoted experimental error (0.5%) any compositional dependence of the partial molar volumes of SiO_2 and $NaAlSi_3O_8$ vanishes. Similarly in the two-component systems Na_2O - SiO_2, K_2O - SiO_2, CaO - SiO_2, and MgO - SiO_2 studied by Bockris et al. (1956) and Tomlinson et al. (1958), no compositional dependence of $\bar{v}_i$ of the oxides can be seen within the precision of replicate experiments (up to 1.1%). Thus, these data suggest that the partial molar volumes of oxide components in these silicate liquids are independent of composition within the experimental error of density measurement. There will also be an error arising from the uncertainties in the composition of each liquid, which Bockris et al. (1956) estimate as 0.07%, but present no data to support this. Only one in four of their compositions was analyzed, and these contained up to 0.7 weight percent CO_2. As the precision of the best chemical techniques of the analysis of oxide components in silicates 0.4 to 2% (Carmichael et al., 1968) depending on their concentration, we estimate a total error of 1-2% arising from error in measurement and composition.

The partial molar volumes of the oxide components in silicate liquids have been calculated using the relationship

$$V = \Sigma \bar{v}_i X_i \qquad (2)$$

where V is the volume of a gram formula weight of the liquid, obtained by multiplying the specific volumes given in Table II by the gram

formula weights (Table I) of the respective compositions, $\bar{v}_i$ is the partial molar volume of component i and X_i is the mole fraction of component i.

By combining the specific volumes for 20 liquids (Table II, excluding the Kilauea basalt, Ki12), multiplied by their respective gram formula weights, with the 96 sets of published data (Shartsis et al., 1952; Bockris et al., 1956; Tomlinson et al., 1958; Barrett and Thomas, 1959; Henderson, 1964; and Riebling, 1964, 1966), values of $\bar{v}_i$ at five temperatures were obtained using the Statistical Package for the Social Sciences multiple linear regression program in the SPSS version 7.0 software package (Nie et al., 1975). The regressed values of $\bar{v}_i$ for eight oxide components at five different temperatures are given in Table III. At each temperature the multiple r^2 value was greater than 0.9994 for the 116 sets of data, and the largest standard deviation of the residuals of the regression equation was 0.551, which corresponds to 1.8% of the molar volume at each temperature. This value of 1.8% is close to our estimate of the overall errors for the typical measurement (1 -2%), so that any compositional dependence of $\bar{v}_i$ is not presently warranted, and the use of multiple linear regression is justified. Since only Henderson (1964) has determined specific volumes for compositions containing Fe_2O_3 and because the mole fractions of Fe_2O_3 in his liquids were never greater than 0.0146, we made no attempt to calculate the partial molar volume of Fe_2O_3. For all compositions that contained Fe_2O_3, the recommendation of Bottinga and Weill (1970) that $\bar{v}_{Fe_2O_3} = 50.32 + 1.02 \times 10^{-3} T$ K (cm^3/mole) was taken. The contribution of Fe_2O_3 to each volume was first subtracted from the molar volume/gfw

before including them in the data set for regression.

The values of $\bar{v}_i$ in Table III were calculated without any weighting, so that with only eight compositions containing TiO_2, the regression coefficient for TiO_2, $\bar{v}_{TiO_2}$, tended to be disproportionately affected by random errors in all of the other components. The value of the standard error for $\bar{v}_{TiO_2}$ (Table III) is larger, in our opinion, than the error from the experiments and the uncertainties in the compositions. Thus another regression was performed after weighting, somewhat arbitrarily, the data in this manner: weighting factors were determined from the reciprocal of the number of two, three, four and five-component liquids in the data set. The weighted partial molar volumes (Table III) (obtained again through multiple linear regression) lie within the bounds of the unweighted $\bar{v}_i$'s. The notable difference between the two sets of coefficients is that the standard errors for partial molar volumes of the oxides are much less in the weighted set, particularly for TiO_2.

Bottinga and Weill (1970) have calculated the partial molar volumes of oxide components in silicate liquids using substantially the same data set less our new results which include TiO_2 as a component. However, they used a stepwise technique, in that they used binary systems to derive the appropriate partial molar volumes of two components and then with these two values known, the $\bar{v}$ of a third component in a ternary system was calculated. As our method of regression, weighted or unweighted, treated all of the data simultaneously, it is not surprising that the two sets of calculated partial molar volumes differ. This is shown in Figure 2, where our unweighted partial molar volumes,

plotted with two standard errors on either side of the mean value, are shown as a function of temperature; the respective values of Bottinga and Weill (1970) are also plotted. Overall the agreement between our results and those of Bottinga and Weill is good, the major differences resulting from the different regression techniques used. $\bar{v}_{Al_2O_3}$ is significantly lower than Bottinga and Weill's value below 1600°C, and has a greater temperature dependence; similarly $\bar{v}_{CaO}$ also has a greater temperature dependence. Our values for $\bar{v}_{SiO_2}$ show no statistically significant change with temperature. Bottinga and Weill's estimate of the value of $\bar{v}_{TiO_2}$ (i.e., from anatase) is within the errors of our calculated value for the unweighted data.

From the partial molar volumes given in Table III, thermal expansions of $\bar{v}_i$ can be calculated. These are not strictly partial molar expansivities, for they were calculated from the relationship $(1/\bar{v}_i)(\partial\bar{v}_i/\partial T)_P$, rather than from regression of $(1/V)(\partial V/\partial T)_P$ for each liquid composition. In general it is experimentally difficult to obtain precise values of a differential property, e.g., thermal expansion and compressibility, from an integral property such as volume. Nevertheless, calculated values of the thermal expansion of the partial molar volumes are given in Table IV, which are consistent with the volumes given in Table III. Unlike the typical behavior of thermal expansion of silicate solids, the values for silicate liquids show a decrease with temperature, although this difference could arise solely because of the experimental assumption that buoyancy is a linear function of temperature.

EVIDENCE FOR EXCESS VOLUME IN SILICATE LIQUIDS

The excess volume of a component in a phase, in this case a silicate liquid, is defined as

$$\bar{v}_i^{xs} = \bar{v}_i - V_i^o$$

where $\bar{v}_i$ is the partial molar volume of the i component, and V_i^o is the molar volume of the pure component i at the same temperature and pressure. If $\bar{v}_i^{xs}$ is zero, i can be said to mix ideally with respect to volume.

Experimentally it has proven difficult to measure density of pure liquid oxide components, for they may decompose at high temperatures (e.g., K_2O) or they may melt at temperatures which are so high (e.g., MgO, 3125 K) that they are normally inaccessible to measurement. Furthermore, the change of density with temperature must be well known if the values of liquid oxide densities are to be extrapolated down into their metastable region appropriate to the temperatures (1523 -1873 K) of the multi-component silicate liquids of this investigation.

However, a less rigorous test of excess volume is available, namely that with the partial molar volumes derived from two or more component silicate systems (Table III) it should be possible to calculate, within analytical uncertainty, the volume/gfw of complex silicate liquids such as those occurring in nature. We have measured the density of a Kilauea basaltic liquid (Tables I and II). In Table V, the measured values of volume/gfw are compared wiith the calculated values using the unweighted data of Table III. Furthermore, Murase and McBirney (1973) have measured the liquid densities of five lava compositions.

However, in only two of these is the oxidation state of Fe known in the liquid, and for their two compositions run in Fe crucibles, the measured and calculated values of volume agree to within 1% (Table V). In the calculations $\bar{v}_{MnO}$ was taken equal to that of $\bar{v}_{FeO}$, and the contribution of P_2O_5 to the liquid volume was ignored, for it is present in only trivial amounts. However, although the agreement between the calculated volumes/gfw using the weighted partial molar volumes (Table III) is slightly better than for the unweighted data when compared to two of the three liquids (Table V), the comparison with the volume of the synthetic lunar liquid is less good, presumably because of TiO_2 which was weighted heavily in the regression. For this reason we have used the unweighted data throughout.

The concordance over the compositional range of basalts and lunar basalts, between measured and calculated values of volume, is necessary but not sufficient evidence for the absence of excess volume, or alternatively for the partial molar volumes not being compositionally dependent within the investigated range of temperature and composition. Additional evidence is given in Table VI, where the value of V_i^o is given for $CaMgSi_2O_6$ and Fe_2SiO_4 liquids at their 1-bar melting temperatures. The values of V_i^o have been calculated from the relationship

$$(dT/dP)_{T_m\,,\,1\ bar} = T_m \Delta V_m^o / \Delta H_m^o$$

where dT/dP is the initial slope of the fusion curve, ΔV_m^o and ΔH_m^o are the volume and heat of melting respectively, and T_m is the melting temperature of the pure solid compound of interest at 1 bar. Values of ΔH_m^o are known for both diopside and fayalite (Weill et al., 1979;

Orr, 1953), as are the slopes of their fusion curves (Table VI) so that if it can be demonstrated, for the example of $CaMgSi_2O_6$, that ΔV_m^o calculated from the Clapeyron slope is equal to ΔV_m calculated from the volume data of Table III, then for this component $\Sigma \bar{v}_i = V_i^o$ Formally the equation is

$$V_m = (\bar{v}_{CaO} + \bar{v}_{MgO} + 2\bar{v}_{SiO_2}) - V^o{}_{solid}$$

and as can be seen in Table VI, the agreement between $\Sigma\bar{v}_i$ and V_i for the components Fe_2SiO_4 and $CaMgSi_2O_6$ is satisfactory. This again suggests that multi-component silicate liquids mix ideally with respect to the volume of their components.

However, as volume is an integral property, it will not be the most sensitive property to illustrate the behavior of silicate liquids on mixing. For this purpose, compressibility measurements, which can be made directly using ultrasonic techniques, should be the more reliable. The individual results of Bockris and Kojonen (1960) and Baidov and Kunin (1968) show a considerable dependence of compressibility on composition in the system K_2O - SiO_2, but the two sets of data at the same temperature show such a large scatter that any conclusion is uncertain. The compressibility of silicate liquids as a function of temperature and composition is presently being investigated in our laboratory.

Overall we conclude that within a 1 - 2% uncertainty, and within the temperature and composition range studied, there is no secure evidence for a compositional dependence of $\bar{v}_i$, or alternatively there is no evidence for an excess partial molar volume. This suggests that, until measurements are made of compressibility, multi-component

silicate liquids may be considered to mix ideally with respect to volume. As there is a heat of mixing (Weill et al., 1979) but no excess heat capacity (Carmichael et al., 1977) in multi-component silicate liquids, they perhaps may be treated as regular solutions.

SUMMARY AND CONCLUSIONS

Density measurements have been carried out on synthetic silicate liquids. These measurements, when combined with density values reported in the literature for 96 other compositions, are used to calculate partial molar volumes of oxide components in silicate liquids. These calculated partial molar volumes can be used to calculate the volumes/gfw or densities of naturally occurring compositions to a precision of about the same as the experimental error. Within the range of temperature and composition of the data set, silicate liquids mix ideally with respect to volume within a 1 - 2% experimental error, a conclusion also reached by Bottinga and Weill (1970). This conclusion should not be used to support theories of silicate liquid structure until more measurements of compressibility as a function of temperature and composition are available.

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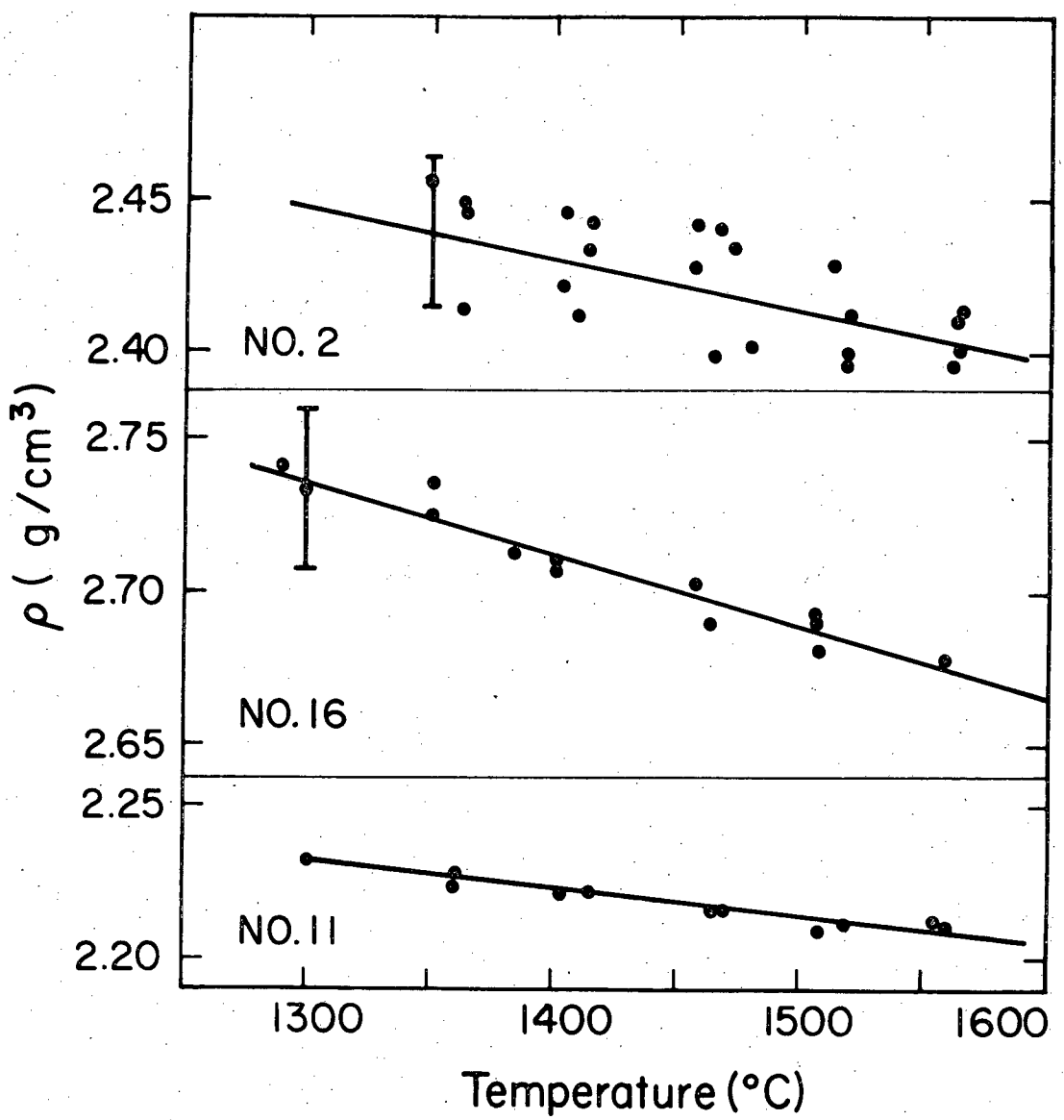
FIGURE CAPTIONS

Fig. 1 Three examples of the raw density data for the indicated compositions, showing the best fit line determined by least squares. Error bar represents ± 1% at the indicated position.

Fig. 2 Partial molar volumes of eight oxide components from Table II. Shaded region represents ±2 standard errors about the mean for the unweighted data. Dots are the values reported by Bottinga and Weill (1970).



XBL 796-1743

Figure 1

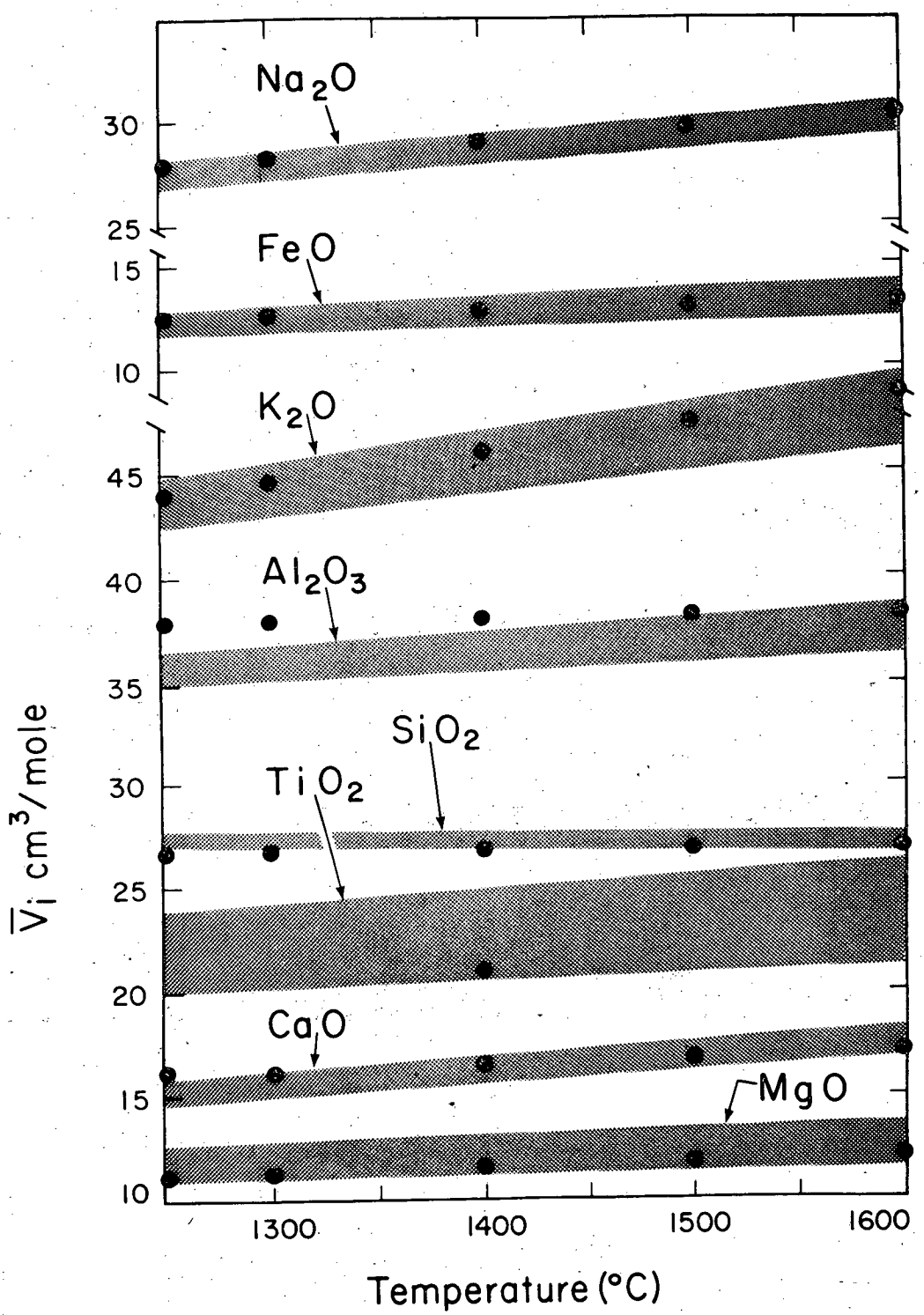


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Figure 2

TABLE I

CHEMICAL ANALYSES OF LIQUID COMPOSITIONS (Wt %)

	NS	KS	1	2	4	6	7	8	9	10	11
SiO_2	48.80	70.33	51.33	59.84	45.98	52.85	39.76	51.35	72.74	62.85	64.06
TiO_2	-	-	13.96	-	-	20.29	-	15.20	-	-	-
Al_2O_3	-	-	15.65	18.81	17.15	-	10.45	-	-	-	-
Fe_2O_3	-	-	-	-	-	-	0.81	-	-	-	-
FeO	-	-	-	-	-	-	43.40	-	-	-	-
MnO	-	-	-	-	-	-	-	-	-	-	-
MgO	-	-	-	4.74	7.80	-	-	-	8.20	13.41	9.78
CaO	-	0.28	14.02	10.04	28.80	-	5.45	-	0.14	0.21	0.12
Na_2O	51.33	-	5.10	6.27	-	26.83	-	33.56	-	23.86	-
K_2O	-	28.07	-	-	-	-	-	-	18.42	-	26.22
P_2O_5	-	-	-	-	-	-	-	-	-	-	-
TOTAL:	100.13	98.40	100.06	99.70	99.73	99.97	99.87	100.11	99.50	100.33	100.18
gfw*	61.041	67.971	66.055	63.173	60.791	63.821	67.625	63.108	61.721	56.765	63.035

(Continued)

TABLE I (Contd.)

	12	13	14	15	16	17	20	21	22	Ki12
SiO_2	67.90	61.76	31.53	60.36	45.90	56.86	57.01	41.69	36.80	49.67
TiO_2	-	-	43.00	-	10.64	-	11.82	4.56	8.75	2.91
Al_2O_3	17.03	-	-	21.47	13.22	9.20	17.21	35.71	12.48	13.49
Fe_2O_3	-	-	-	-	-	-	-	-	-	-
FeO	-	-	-	-	-	-	-	-	12.02	14.24
MnO	-	-	-	-	-	-	-	-	-	0.18
MgO	-	20.69	-	-	-	10.77	-	-	7.40	5.94
CaO	-	16.95	25.22	-	30.15	13.21	-	17.67	0.20	9.72
Na_2O	12.55	-	-	11.25	-	9.94	13.95	-	8.01	2.56
K_2O	-	-	-	6.44	-	-	-	-	14.15	0.68
TOTAL:	99.28	99.40	99.75	99.52	99.91	99.98	99.99	99.63	99.81	99.68
gfw*	64.908	53.920	65.943	67.931	63.866	60.784	67.079	70.348	67.517	63.596

*The gram formula weights (gfw) of each composition were calculated by multiplying the mole fractions of each oxide by its respective molecular weight as tabulated by Carmichael et al. (1977). Note that all liquids (except those containing Fe) contained about 190 - 210 ppm PtO_2.

TABLE II

SPECIFIC VOLUMES OF COMPOSITIONS STUDIED

$V = a + bT$ K

Composition	a cc/g	$bx10^5$ cc/gK	Composition	a cc/g	$bx10^5$ cc/gK
NS	0.3626	5.163	11	0.4207	1.753
KS	0.4348	1.555	12	0.3464	4.288
1	0.3421	3.456	13	0.3614	1.561
2	0.3542	3.360	14	0.2284	6.262
4	0.3378	1.987	15	0.3935	2.889
6	0.3287	5.949	16	0.3138	3.271
7	0.2103	7.263	17	0.4141	0.282
8	0.3450	4.806	20	0.3838	1.662
9	0.4259	0.635	21	0.3579	1.456
10	0.3756	2.501	22	0.3153	3.973
			Ki12	0.3021	3.973

TABLE III

PARTIAL MOLAR VOLUMES OF OXIDE COMPONENTS IN SILICATE LIQUIDS

cc/mole - Numbers in parentheses represent one standard error

	1250°C	1300°C	1400°C	1500°C	1600°C
Unweighted					
SiO_2	27.26(0.18)	27.24(0.18)	27.19(0.18)	27.16(0.22)	27.12(0.27)
TiO_2	21.71(1.05)	22.02(1.02)	22.63(1.06)	23.24(1.25)	23.84(1.54)
Al_2O_3	35.45(0.44)	35.71(0.43)	36.23(0.44)	36.80(0.52)	37.37(0.65)
FeO	12.25(0.32)	12.39(0.31)	12.60(0.30)	12.92(0.38)	13.19(0.47)
MgO	11.79(0.40)	11.90(0.39)	12.09(0.41)	12.28(0.48)	12.46(0.60)
CaO	15.19(0.28)	15.51(0.27)	16.16(0.28)	16.80(0.33)	17.45(0.41)
Na_2O	27.51(0.30)	27.87(0.29)	28.57(0.30)	29.28(0.36)	29.97(0.44)
K_2O	43.70(0.66)	44.31(0.64)	45.50(0.67)	46.69(0.79)	47.87(0.97)
Weighted					
SiO_2	27.20(0.14)	27.18(0.13)	27.14(0.14)	27.11(0.16)	27.07(0.19)
TiO_2	23.57(0.59)	23.84(0.57)	24.37(0.58)	24.88(0.66)	25.36(0.80)
Al_2O_3	35.85(0.32)	36.11(0.31)	36.64(0.32)	37.21(0.36)	37.79(0.44)
FeO	12.38(0.23)	12.60(0.22)	12.97(0.22)	13.48(0.26)	13.92(0.31)
MgO	12.17(0.32)	12.16(0.31)	12.15(0.32)	12.13(0.37)	12.12(0.44)
CaO	15.21(0.23)	15.52(0.22)	16.15(0.23)	16.77(0.26)	17.42(0.31)
Na_2O	27.54(0.26)	27.88(0.25)	28.56(0.26)	29.24(0.30)	29.92(0.36)
K_2O	45.17(0.54)	45.68(0.52)	46.66(0.53)	47.67(0.60)	48.69(0.73)

TABLE IV

THERMAL EXPANSIONS OF THE PARTIAL MOLAR VOLUMES

$\bar{\alpha}_i = a + bT$ K

	$a \times 10^4$	$b \times 10^8$
TiO_2	3.87	-7.07
Al_2O_3	1.89	-2.24
FeO	2.86	-4.40
MgO	1.98	-2.43
CaO	6.58	-15.40
Na_O	3.45	-5.93
K_2O	3.73	-6.67

SiO_2 is not included as $d\bar{v}_{SiO_2}/dT = 0$ within the error reported in Table III.

TABLE V

COMPARISON OF MEASURED WITH CALCULATED VOLUMES (cm^3/gfw)

FOR NATURALLY OCCURRING LIQUIDS

	1573 K		1673 K		1773 K	
Kilauea basalt (Tables I and II)	Unwtd.	Wtd.	Unwtd.	Wtd.	Unwtd.	Wtd.
Measured	23.19	23.19	23.44	23.44	23.69	23.69
Calculated (Table III)	23.25	23.25	23.42	23.52	23.62	23.72
% difference	+0.3	+0.7	-0.1	+0.3	-0.3	+0.1
Columbia River basalt Murase and McBirney (1973) (run in Fe crucibles)						
Measured	23.88	23.88	24.06	24.06	-	-
Calculated	23.71	23.79	23.87	23.97	-	-
% difference	-0.7	-0.4	-0.8	-0.4	-	-
Synthetic lunar sample Murase and McBirney (1973) (run in Fe crucibles)						
Measured	21.52	21.52	21.59	21.59	-	-
Calculated	21.59	21.81	21.78	22.00	-	-
% difference	+0.3	+1.3	+0.9	+1.9	-	-

TABLE VI

CALCULATED VALUES OF $\Delta V^o(V_L^o - V_S^o)$ OF FUSION AND COMPARISON WITH $\Sigma(\bar{v}_i)_L - V_S^o$ USING LIQUID OXIDE COMPONENTS (Table III)

	$(dT/dP)_{1\ bar}$	ΔH_m cals.	ΔV_m^o cals./bar	$\Sigma(\bar{v}_i)_L - V_S^o$ cals./bar	% Diff.
$CaMgSi_2O_6$	0.0157	34085	0.3215±0.004	0.3248	-1.0
Fe_2SiO_4	0.0062	22030	0.0917±0.004	0.0887	+3.3

Data from Rosenhauer and Eggler (1975), Weill et al., (1979), Orr Lindsley (1967), Skinner (1966), Boyd and England (1963).

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