

## Melt densities in the $\text{Na}_2\text{O-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ system and the partial molar volume of tetrahedrally-coordinated ferric iron in silicate melts

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**Abstract**—The densities of 12 melts in the  $\text{Na}_2\text{O-FeO-Fe}_2\text{O}_3\text{-SiO}_2$  system have been determined in equilibrium with air, in the temperature range of 1000–1500°C, using the double bob, Archimedean technique. Ferrous iron determinations of 100–200 mg samples, “dip” quenched from high temperature, indicate that all the melts investigated were highly oxidized under these experimental conditions. <sup>57</sup>Fe Mössbauer spectra of glasses obtained by drop quenching 80 mg melt samples from loop equilibration runs yield  $\text{Fe}^{3+}/\text{Fe}^{2+}$  data equivalent to that for the densitometry (dip) samples for all but the most viscous melt, and confirm that all but one melt equilibrated with air during the densitometry measurements.

Melt densities range from 2.17 to 2.88 g/cm<sup>3</sup> with a mean standard deviation (from replicate experiments) of 0.36%. Least squares regression of the density data at 1300, 1400 and 1500°C, was calculated, both excluding and including excess volume terms (herein named linear and nonlinear fits, respectively) and the root mean squared deviation (RMSD) of each regression was compared with the total experimental error. The partial molar volumes computed for linear fits for  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  are similar to those previously reported for melts in the  $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$  system (STEIN *et al.*, 1986). The partial molar volumes of  $\text{Fe}_2\text{O}_3$  obtained in these linear fits are equal to those obtained by SHIRAIISHI *et al.* (1978) in the  $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$  system but 5 to 10% lower than reported by MO *et al.* (1982) in multicomponent melts. The partial molar volume exhibited by  $\text{Fe}^{3+}$  in this system is representative of the partial molar volume of tetrahedrally coordinated  $\text{Fe}^{3+}$  in silicate melts.

### INTRODUCTION

THE ROLE OF the oxidation state of silicate melts in the petrogenesis of igneous rocks has received increasing attention in recent years due to several advances in our understanding of the behavior of iron in silicate melts. Investigations of the structural role of iron in silicate melts continue to clarify the effect of redox equilibria on melt structure (*e.g.* FOX *et al.*, 1982; HENDERSON *et al.*, 1984; VIRGO and MYSEN, 1985; MYSEN *et al.*, 1985; GOLDMAN, 1986). In addition, several studies have broadened our knowledge of the composition-dependence of redox equilibria in simple and complex silicate melts (DICKENSON and HESS, 1981, 1986a,b; MYSEN *et al.*, 1985; SACK *et al.*, 1980; KILINC *et al.*, 1983) and, as a result, models for the prediction of homogeneous equilibria involving iron in igneous melts have been proposed (SACK *et al.*, 1980; KILINC *et al.*, 1983; MYSEN, 1988). In addition, studies of the relationship between redox state and the physical properties of silicate melts continue to provide tests for models of the relationship between the molecular structure and the macroscopic properties of silicate melts (*e.g.* density, MO *et al.*, 1982; LICKO *et al.*, 1985; DINGWELL and BREARLEY, 1987; viscosity, TOGURI *et al.*, 1976; SEKI and OETERS, 1984; DANEK *et al.*, 1985; DINGWELL and VIRGO, 1987; oxygen diffusion, CANIL and MUEHLENBACHS, 1987).

Recent observations of Mössbauer spectra of ferric iron in silicate glasses have been interpreted to indicate the presence of more than one coordination geometry for this cation (MYSEN *et al.*, 1985; VIRGO and MYSEN, 1985). The shift of ferric

iron Mössbauer parameters as functions of the bulk composition and of the redox state of silicate melts has prompted the suggestion that partial molar properties of ferric iron in these melts might vary with composition in a way that is significant for geologic calculations. One such property, the partial molar volume of ferric iron, is the subject of this study.

Recent areas of investigation in the geological literature that emphasize the continuing need for more and better density data on iron-bearing silicate melts include the following. Firstly, the estimation of the pressure-dependence of redox equilibria in igneous melts is necessary to make inferences regarding the oxidation state of magma source regions from a knowledge of their redox state upon eruption (*e.g.* CARMICHAEL and GHIORSO, 1986). Secondly, the calculation of spatial density gradients in magma chambers resulting from compositional variations can provide tests for the evaluation of the style and magnitude of convection in these chambers (*e.g.* HUPPERT and SPARKS, 1980; CAMPBELL and TURNER, 1986). Thirdly, the density of the melt is an input parameter in deriving the melt-buffer rod interface reflection coefficient necessary to constrain wave amplitudes in ultrasonic studies of silicate melts and to calculate compressibilities from wave velocity data in these studies (*e.g.* MANGHNANI *et al.*, 1986; RIVERS and CARMICHAEL, 1987; KRESS *et al.*, 1988).

For iron-bearing melts, these types of calculations require accurate partial molar volume data for ferric and ferrous iron. Previous work on the partial molar volume of ferric iron by MO *et al.* (1982) was performed with the intent of deriving a widely applicable input parameter for calculations involving natural (>10 component) systems. Thus the work of MO *et al.* (1982) involved 8 compositions in an 11 component system. As stated at that time, the data obtained were insufficient to test conclusively for composition-dependence of the partial

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molar volume of ferric iron. In addition, it now appears that the redox characterization of these melts was inadequate (LANGE and CARMICHAEL, 1987). The inadequacy of the existing data base has been emphasized more recently by BOTTINGA *et al.*, (1983; 1984) and VIRGO and MYSEN (1985) who appeal for data to fill the gap in our knowledge of simple systems.

The present work in the  $\text{Na}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  system was conducted with the intent of providing a datum for a test of the composition-dependence of the partial molar volume of ferric iron and to augment the data base for calculational schemes (BOTTINGA and WEILL, 1970; BOTTINGA *et al.*, 1982; LANGE and CARMICHAEL, 1987) for predicting melt densities where ferric iron is abundant.

The  $\text{Na}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  system is well-suited to this task for the following reasons. Firstly, previous investigations of the structural role of ferric iron in melts in this system have suggested that, under the  $T - f\text{O}_2$  conditions of the present study, the coordination of ferric iron is composition-independent, consisting of  $\text{NaFeO}_2$  tetrahedra (DANCKWERTH and VIRGO, 1982). Secondly, the liquidus phase equilibria of this system indicated that a very large range of compositions would be experimentally accessible (*i.e.*, densities could be obtained over a reasonable temperature range, BOWEN *et al.*, 1930). Thirdly, this system contains the acmite component, which is a major normative component of intermediate to acidic peralkaline rocks, precisely those igneous

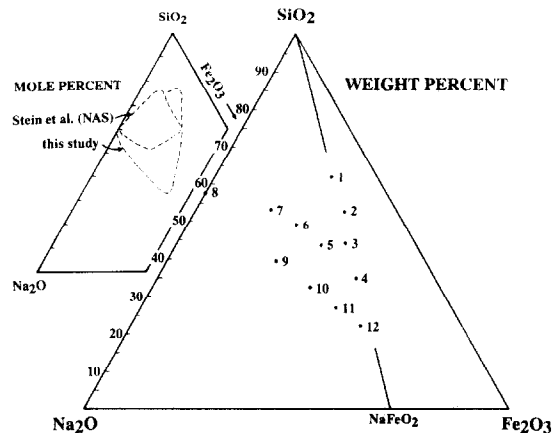


FIG. 1. The electron microprobe analyses of the compositions investigated in this study plotted in the system  $\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  in wt%. Also, a comparison of the range of molar proportions of  $\text{Na}_2\text{O}$ , ( $\text{Al}_2\text{O}_3$  or  $\text{Fe}_2\text{O}_3$ ) and  $\text{SiO}_2$  in this study and STEIN *et al.* (1986).

rocks whose melts are anticipated to contain abundant ferric iron in tetrahedral coordination due to a shortage of aluminum.

## EXPERIMENTAL METHOD

### Sample preparation

The starting materials for the densitometry experiments were synthesized in air by direct fusion of reagent grade  $\text{Na}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$  and purified quartz sand. The  $\text{Na}_2\text{CO}_3$  and  $\text{Fe}_2\text{O}_3$  were dried at  $300^\circ\text{C}$  and the quartz sand was dried at  $120^\circ\text{C}$  prior to mixing. One thousand gram batches of compositions 1 through 8 were fused in silica crucibles at  $1600^\circ\text{C}$  for 1 hour. One hundred gram batches of the high-sodium samples 9 through 12 were fused in platinum crucibles at  $1400^\circ\text{C}$  for 30 min. The fused samples were poured onto steel plates for cooling. The iron-bearing starting glasses were analysed by electron microprobe for composition and homogeneity. The microprobe analyses utilized mineral standards: jadeite for Na, magnetite for Fe and grossular for Si. Static beam volatilization tests (reanalysis of spots and monitoring of count rates) indicated that Na loss was not a problem for these glasses. As an additional precaution, we used a defocused beam (20–50 microns) and moved the samples under the beam during analysis to avoid Na loss. The results of analyses are presented in Table 1 and Fig. 1 and the analytical errors are discussed in the Results section of this paper. Each composition is the mean of six analyses, and homogeneity within the microprobe errors was observed. Iron-free sample 8 was unstable under the electron microprobe beam and was analysed instead by neutron activation for Na and by X-ray fluorescence for Si (the results of this analysis are included in Table 1 and Fig. 1). The microprobe totals for the Si-poor glasses are slightly high (approx. 102%) possibly due to increasingly large ZAF corrections for these samples but the 100% normalization of the analyses of the most Si-poor glasses used in the study yielded compositions within error of the original "weighed in" compositions.

As a check against compositional drift during the densitometry experiments, samples of glass obtained before and after the experiments were compared in composition using the electron microprobe. As had been previously observed during viscometry experiments on equivalent sized melt samples in this system (DINGWELL and VIRGO, 1987; 1988), no compositional drift was observed. The ferric/ferrous ratios of the melts investigated were obtained at each temperature of density measurement as discussed below.

The melt densities were determined using the double-bob Archimedeian technique. The apparatus used is similar to that of BOCKRIS *et al.* (1956) and is depicted in Fig. 2. We have added an iris diaphragm to assist furnace closure and an alumina bumper to prevent bob-

Table 1. Analyses of glasses. (wt%)

Sample	$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{Fe}_2\text{O}_3^1$	$\text{FeO}^2(\text{H})$	$\text{FeO}(\text{M})$	$\text{FeO}(\text{L})$
1	62.04	10.31	27.73	3.57 (0.33)	3.34 (0.10)	3.25 (0.11)
2	52.82	12.65	35.22	3.42 (0.24)	2.98 (0.18)	1.92 (0.12)
3	44.29	16.55	40.15	4.24 (0.16)	2.98 (0.19)	1.86 (0.15)
4	40.61	19.21	42.75	4.57 (0.11)	2.66 (0.15)	1.71 (0.10)
5	43.95	22.71	34.63	3.30 (0.11)	1.10 (0.11)	0.46 (0.08)
6	49.46	25.77	25.93	2.37 (0.14)	0.71 (0.09)	0.90 (0.08)
7	52.86	29.52	17.66	1.98 (0.11)	0.50 (0.29)	0.19 (0.07)
8	57.60	41.93				
9	38.49	34.45	25.98	0.97 (0.21)	0.13 (0.03)	0.00
10	32.76	30.72	36.85	1.41 (0.02)	0.33 (0.04)	0.05 (0.04)
11	29.54	28.30	44.36	1.30 (0.10)	0.33 (0.03)	0.03 (0.01)
12	22.68	24.77	55.34	2.16 (0.10)	2.39 (0.05)	0.92 (0.05)
drop quench data <sup>3</sup>			<sup>4</sup> $\text{FeO}(1300)$	$\text{FeO}(1400)$	$\text{FeO}(1500)$	
1			1.36	2.79	3.74	
2			1.53	3.02	5.33	
3			1.49	2.61	4.19	
4			2.03	3.09	4.44	
5			0.78	1.56	2.81	
6			0.49	1.06	2.05	
7			0.45	0.92	1.70	
8						
9			0.34	0.87	1.96	
10			0.31	0.93	2.40	
11			0.51	1.21	2.56	
12			0.30	1.15	3.61	

<sup>1</sup> total iron reported as  $\text{Fe}_2\text{O}_3$  in microprobe analyses (15kV, 3nA).

<sup>2</sup> FeO determinations for the high (H), medium (M) and low (L) temperature dip samples. Numbers in brackets are 1 std. dev. in replicate determinations.

<sup>3</sup> FeO data from least squares fits to the  $^{57}\text{Fe}$  Mössbauer spectra-derived ferric/ferrous ratio as a function of reciprocal absolute temperature.

<sup>4</sup> Errors in Mössbauer analyses of area ratios correspond to  $\pm 2\%$  of ferric/total iron.

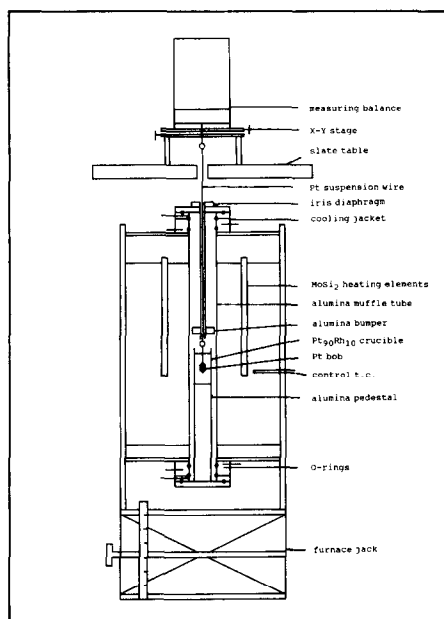


FIG. 2. A schematic drawing of the apparatus used in the present study for the determination of melt densities. The balance is precise to  $\pm 0.0001$  g and the vertical positioning is precise to 0.2 mm.

crucible contact. The previously fused starting materials were remelted into rigid, cylindrical, Pt<sub>90</sub>Rh<sub>10</sub> crucibles (2.54 cm inner diameter, 5.08 cm height, 1 mm wall thickness) and bottom-loaded into a vertical (3.5 cm inner diameter) tube furnace. The samples were supported in the hot zone of the furnace by an alumina tube (2.54 cm outer diameter) pedestal. Hot zone temperature was maintained with an electronic set-point controller and a Pt<sub>94</sub>Rh<sub>6</sub>-Pt<sub>70</sub>Rh<sub>30</sub> control thermocouple and monitored with a Pt-Pt<sub>90</sub>Rh<sub>10</sub> thermocouple (checked periodically against the melting point of Au). The measuring thermocouple was sheathed in a Pt sleeve and immersed in the melt sample before and after each density determination. We estimate the maximum temperature uncertainty including contributions from thermal gradients and time fluctuations at  $\pm 2^\circ\text{C}$ . The tube furnace (heated by MoSi<sub>2</sub> hairpin elements) was mounted on a screw jack which permitted vertical positioning of the furnace and sample to a precision of 0.2 mm over a range of 15 cm. A 75 kg weighing table above the tube furnace supports an "X - Y" centering stage designed to position the weighing balance over the furnace. The centering stage is also fitted with a clutch mechanism that permits the entire stage to be slid away from the furnace. This mechanism along with a sliding block in the table permit easy vertical access to the furnace top. The balance employed is a digital model Mettler AE100. The automatic taring feature of this balance was used to obtain direct buoyancy readings.

The bobs used for immersion were fabricated from pure platinum in the form of spindles whose cross-sections are depicted in Fig. 2. The bobs were suspended from 0.5 mm dia. platinum wire leaders which were, in turn, suspended from thicker platinum wire lengths that extended out of the furnace. The thin leaders were used to minimize errors in immersed mass due to uncertainty in the immersion depth of the leader wire. Closure at the top of the furnace is accomplished with a (0.1 to 3 cm) iris diaphragm.

The masses of the bobs (corrected for air) were measured prior to this study and at regular intervals during the buoyancy determinations. The high-temperature submerged volumes of the bobs were computed from their known masses, the S.T.P. density of platinum, the thermal expansion coefficient of platinum, and geometric considerations for the immersed length of leader wire and the melt height displacement of the immersed bob.

The experiments were conducted in sets of 6 separate immersions at each of 3 temperatures (generally ranging from 1500°C to the liquidus) for each composition. The large and small bobs were each

immersed three times in the melt and the mean of the three buoyancy determinations was computed for each. The difference between the two means was entered into a computer routine which solved for melt density using equation (1) and  $T - V$  data for pure platinum (EDWARDS *et al.*, 1951; WASEDA *et al.*, 1975).

$$\text{Density} = (B_1 - B_2)/(V_1 - V_2) \quad (1)$$

where  $B_1$  and  $B_2$  are the buoyancies and  $V_1$  and  $V_2$  are the submerged volumes of the large and small bobs, respectively.

#### Precision and accuracy

The precision of the above technique was taken as the standard deviations obtained from the three replicate buoyancy determinations for the large and small bobs propagated through Eqn. (1) using the square root of the sum of the squares. The individual precisions are reported (in Table 2) for each temperature and composition and the mean of these is 0.36% of the measured density.

The accuracy of the present work was tested in two ways. Firstly, the density of molten NaCl (6 replicates) was measured at 1063°C to be 1.4150 g/cc in excellent agreement (0.17% high) with the value of 1.4125 g/cc computed from the density-temperature relationship given by JANZ (1980). The density of molten NaCl was redetermined after the completion of this study (involving over 200 immersions) in order to access the effect of iron contamination on the density of the platinum bobs. The post-study redetermination of the density of NaCl (1063°C) was 1.4152 gm/cc, virtually identical to the previous determination and within error (0.19% high) of the value from JANZ (1980). The agreement of the two determinations of the density of molten NaCl proves that iron contamination of the platinum bobs has no observable effect on the density of the platinum bobs as thus the density determinations of this study. A similar conclusion was reached by MO *et al.* (1982) based on microprobe analysis of their suspension wire.

#### Redox characterization

After completion of six buoyancy measurements the melt was sampled (4-8 times) by dipping a small (0.4 mm wire, 2-3 mm loop diameter) Platinum wire loop into the sample and quenching the "loop sample" in water. The calculated means of ferrous iron determinations performed on these loop samples using the volumetric vanadate titration method described by WILSON (1960) were taken as representative of the redox state of the melt samples at each tem-

TABLE 2. Melt densities.

Sample	Temp.	Density	Temp.	Density	Temp.	Density
1	1451	2.5144 (.0013) <sup>1</sup>	1349	2.5308 (.0117)	1250	2.5483 (.0181)
2	1439	2.6026 (.0153)	1373	2.6270 (.0039)	1298	2.6279 (.0049)
3	1500	2.6765 (.0101)	1405	2.6973 (.0124)	1300	2.7086 (.0118)
4	1500	2.7202 (.0100)	1399	2.7317 (.0065)	1300	2.7500 (.0063)
5	1497	2.5837 (.0082)	1301	2.6165 (.0043)	1105	2.6723 (.0140)
6	1500	2.4652 (.0085)	1247	2.5162 (.0067)	1002	2.5741 (.0063)
7	1489	2.3584 (.0072)	1251	2.4184 (.0096)	1000	2.4750 (.0130)
8	1480	2.1738 (.0054)	1300	2.2269 (.0091)	1100	2.2823 (.0091)
9	1485	2.4246 (.0198)	1249	2.4811 (.0076)	998	2.5531 (.0054)
10	1480	2.5400 (.0054)	1252	2.6130 (.0025)	1001	2.6748 (.0043)
11	1479	2.6804 (.0026)	1249	2.7492 (.0029)	1020	2.8386 (.0146)
12	1482	2.8558 (.0071)	1403	2.8587 (.0059)	1309	2.8783 (.0035)

<sup>1</sup> numbers in brackets represent 1 standard deviation.

perature of density measurement. These ferrous iron determinations are incorporated into the data of Table 1.

As an additional test of this quenching method and to derive equilibrium redox-temperature relationships for each composition, a series of loop fusion experiments were performed on 80 mg samples of batch glass. The 80 mg samples were equilibrated for 1 hour at 1300, 1400 and 1500°C and drop quenched (by electrically burning off a fine suspension wire) into water. A time series of experiments on sample 1, the most viscous sample in this study (DINGWELL and VIRGO, 1988), indicated that 1 hour was sufficient for equilibration of that sample at 1400°C. The generally observed inverse relationship between oxygen diffusivity and viscosity led us to extend this demonstration of equilibration to the other, less viscous, samples.

Resonant absorption  $^{57}\text{Fe}$  Mössbauer spectra were collected at 25°C with a 50mC  $^{57}\text{Co}/\text{Rh}$  source on powders of the drop-quenched melts from the loop equilibration runs. The powders were contained between sheets of aluminum foil and the absorber thickness was constrained to yield approx. 5 mg Fe/cm<sup>2</sup>. Mirror image spectra were recorded over 512 channels, folded and analysed. The spectral data were deconvoluted with the least-squares fitting routine PC-MOS (copyright CMTE Elektronik, Riemerling, FRG) using Lorentzian lineshapes. The deconvolutions consisted of two doublets, one symmetric doublet assigned to ferric iron and one equal area asymmetric (unequal widths) doublet assigned to ferrous iron. The assignment of doublets in the deconvolution of  $^{57}\text{Fe}$  Mössbauer spectra of glasses in the  $\text{Na}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  system has been discussed at length in previous publications (VIRGO and MYSEN, 1985; DINGWELL and VIRGO, 1987, 1988) and will not be repeated here.

## RESULTS

### Densities

The computed densities derived from 216 buoyancy measurements on 12 melt compositions are reported in Table 2 and shown in Fig. 3. The melt densities range from 2.17 to 2.88 g/cm<sup>3</sup> (a variation of 33%). There is a linear relationship

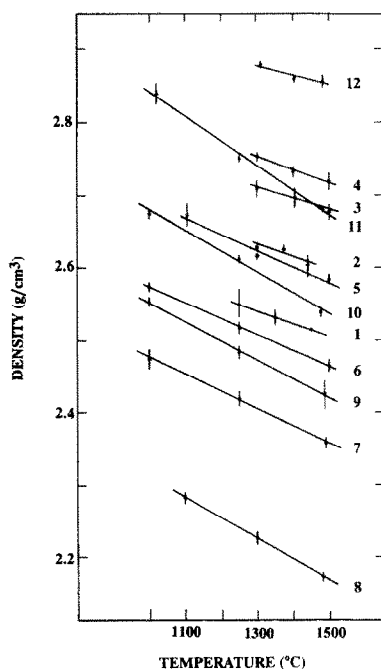


FIG. 3. Compilation of the density data of this study as functions of temperature. All density data have been fitted within error to a linear dependence on temperature. The error bars correspond to 1 standard deviation in the buoyancy determinations propagated through Eqn. (1).

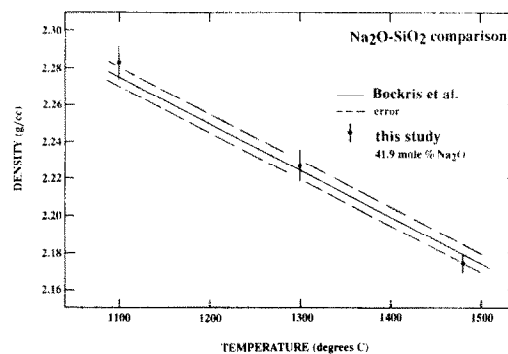


FIG. 4. A comparison of the density determinations of composition 8 of this study (41.9 mole%  $\text{Na}_2\text{O}$ , 58.1 mole%  $\text{SiO}_2$ ) and an interpolation of density determinations by BOCKRIS *et al.* (1956) on  $\text{Na}_2\text{O}-\text{SiO}_2$  melt compositions. The dashed lines represent 1 standard error of the BOCKRIS *et al.* data.

between density and temperature for each composition within the error of the measurements (Fig. 3 and Table 2). At this stage, it is useful to assess the errors involved in both the density measurements and the compositional determinations. The mean error in the precision of our density measurements (propagated as discussed above) is 0.36%. The analytical errors involved in the microprobe analyses are estimated to be less than 1% of the amount present for  $\text{SiO}_2$  and total Fe and less than 2% for  $\text{Na}_2\text{O}$ . The errors in wet chemical analysis for FeO average 2.5% of the amount present. The density measurements and melt compositions were used to calculate the molar volumes of the melts. The above errors propagate into a mean error of 0.55% in the molar volumes of the melts.

Composition 8 of this study is on the  $\text{Na}_2\text{O}-\text{SiO}_2$  binary join and previous density determinations in this binary system are available from BOCKRIS *et al.* (1956). A comparison (of a linear interpolation in composition) of the density-temperature data of these workers and the density-temperature data of composition 8 is illustrated in Fig. 4. The agreement is excellent, well within the precision of the experiments. This agreement also bears on the possibility of iron contamination of the platinum bobs affecting density determinations. Melt composition 8 was investigated after 7 previous compositions involving over 60 previous immersions each of the large and small platinum bobs in melts containing up to 40 wt.% iron. These bobs undoubtedly gained iron from the melts prior to the investigation of composition 8. Despite iron gain, however, the agreement shown in Fig. 4 is further evidence of the insensitivity of the bob densities to iron contamination and further illustrates that comparisons between this work and previous studies in iron-free systems is valid.

### Redox characterization

The results of the wet chemical FeO analyses of dip samples obtained directly from the densitometry batches are presented in Fig. 5 as values of  $\log_{10} (X(\text{Fe}_2\text{O}_3)/X(\text{FeO}))$ . The general behavior of redox ratios as a function of temperature, illustrated in Fig. 5, is a linear dependence on reciprocal absolute temperature (Arrhenius behavior). This type of behavior has been widely observed in equilibrium redox studies of silicate melts and the data of Fig. 5 are reproduced well using the

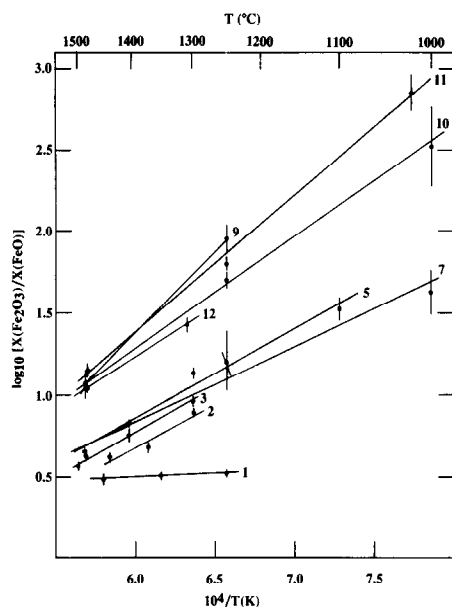


FIG. 5. An Arrhenius plot of dip sample redox ratios for the compositions investigated in this study. The redox ratio has been fitted to a linear function of reciprocal absolute temperature. Two spurious data points in Table 1 have been discarded in this plot. Also, the redox data for compositions 4 and 6 have been omitted for clarity (see data in Table 1).

method of KILINC *et al.* (1983). This agreement leads us to speculate that redox equilibrium was closely approached for the melts 2 to 12.

It is important to note here that the present study does not rely on the complete achievement of redox equilibrium in the melts investigated but rather on a careful monitoring of the actual redox ratios of investigated melts. In order to state that the degree of possible disequilibria does not distort our density-composition analysis (below) we draw attention to two essential observations. Firstly, the buoyancy determinations, which took approximately six hours to complete at each temperature point show no systematic drift in values with time. Secondly, the replication of FeO determinations on multiple melt loop samples at each temperature point showed no variation outside the limits of analytical error of the obtained values. The first point above means that even if the melts were not completely equilibrated during the buoyancy determinations, the possible continuing oxidation of melts during buoyancy determinations had no observable effect (drift) on the buoyancy determinations and thus the computed densities. The second point illustrates that, as the melts were representatively sampled (replicate samples from random depths), no evidence exists for significant melt inhomogeneity in redox state. The observations of constant buoyancy and melt homogeneity obviate the requirement for establishment of redox equilibria in these liquids in order to interpret the results. With this in mind we return to Fig. 5 to point out that compositions 2 to 12 display redox-temperature relationships whose slope and intercept values are closely predicted from equilibrium models; leading us to suggest that these melts very nearly equilibrated. In contrast, composition 1 exhibits a redox ratio that is insensitive to

temperature. The probable cause of this behavior is disequilibria during cooling such that the high temperature redox state was maintained during the entire experiment. Composition 1 is close to NaFeSi<sub>3</sub>O<sub>8</sub> in composition and undoubtedly has the highest viscosity of the samples investigated (DINGWELL and VIRGO, 1988). The generally observed inverse relationship between viscosity and oxygen diffusivity in silicate melts (SHIMIZU and KUSHIRO, 1984) leads us to infer the lowest equilibration rate for this sample due to low oxygen diffusivity.

To test the possibility that the dip sampling technique is incapable (*i.e.*, too slow) of quenching in redox ratios of the less viscous densitometry samples, the results of the loop equilibrated, drop-quenched (into water) samples for each composition are given in Table 1. The redox-temperature relationships for all but sample 1 are in agreement with the dip sample data. This agreement indicates that the redox ratio is insensitive to the difference in quench rate between the drop quench into water and the "dip sample quench". This agreement is also direct evidence that samples 2 to 12 equilibrated during the densitometry runs and that sample 1 did not equilibrate. For sample 1, the equilibrium redox-temperature relationship (from the drop quench samples) intersects the redox-temperature relationship from the actual densitometry sample at approx. 1500°C. Thus the high temperature redox ratio has been metastably preserved to lower temperatures, as postulated above. An unfortunate footnote to the drop quench experiments is that the most Na-rich melts lost Na (as verified by electron microprobe analysis) during 1 hour equilibrations at 1500°C. This was not fully unexpected by the present authors but the effect of this Na-loss on the redox equilibria remains undetermined. We do note that precisely these redox data (those for samples 9, 10, 11, 12 at 1500°C) are more reduced than the equivalent dip quench samples. This last point emphasizes the special difficulties of loop fusion redox equilibrations in alkali-bearing systems and the corresponding utility of dip quenches from large volume samples where equilibrium can be established.

## DISCUSSION

Because the Fe<sub>2</sub>O<sub>3</sub>/FeO of each melt changes with temperature (Fig. 5) we were compelled to analyze our data at three individual temperatures (*cf.*, MO *et al.*, 1982; LICKO *et al.*, 1985) and did not, therefore, independently regress the variation in the partial molar volumes of the oxide components with temperature as may be done in iron-free systems (*e.g.*, STEIN *et al.*, 1986). Also, because our measurements were not conducted at the same temperatures for all liquids, we have interpolated some of the density measurements and Fe<sub>2</sub>O<sub>3</sub>/FeO according to the established relationships (Figs. 3 and 5, Tables 1 and 2) before the regression analysis. The molar volumes and mole fractions of oxide components were regressed at 1300, 1400 and 1500°C using multiple least-squares linear regression according to the following equation:

$$V = \sum_{i=1}^l X_i V_i \quad (2)$$

where  $V$  is the molar volume of the melt,  $X_i$  is the mole fraction of the oxide component and  $V_i$  is the partial molar

volume of the oxide component. The input and results are shown in Tables 3 and 4.

The partial molar volume of FeO was also calculated. However, the computed values had standard deviations larger than the computed partial molar volumes, due to high uncertainties stemming from the low concentrations of FeO in our liquids. A number of measurements and estimations (HENDERSON, 1964; SHIRAISHI *et al.*, 1978; HERZBERG, 1987; LANGE and CARMICHAEL, 1987) of the partial molar volume of FeO are available from the literature and all fall within the range of 13 to 14 cm<sup>3</sup>/mole. This range of values does not significantly affect the computed values of the partial molar volumes of the major components of the compositions of this study and consequently, we constrained the partial molar volume of FeO according to the analysis of HERZBERG (1987). This constraint took the form of subtracting the calculated volume due to FeO from each total volume (*V*, Table 3) to yield an FeO-free volume (*V\**, Table 3). It is important to stress that this constraint, using any reasonable volume for FeO, does not significantly effect the calculated partial molar volumes of the other components. We also wish to stress that we realize excess terms involving FeO may be required to describe the volumes of very FeO-rich melts, our treatment of FeO is an approximation.

TABLE 3. Fit parameters and results.

Sample	X(Na <sub>2</sub> O)	X(SiO <sub>2</sub> )	X(FeO)	X(Fe <sub>2</sub> O <sub>3</sub> )	V	V*	res.
1500 °C							
1	.1190	.7389	.0356	.1065	28.47	28.00	+0.21
2	.1530	.6588	.0459	.1423	28.92	28.31	+0.18
3	.2078	.5736	.0459	.1727	29.22	28.61	-0.12
4	.2411	.5258	.0495	.1835	29.19	28.53	-0.36
5	.2739	.5468	.0343	.1449	29.20	28.74	-0.14
6	.2933	.5806	.0233	.1029	28.87	28.56	-0.11
7	.3221	.5949	.0165	.0665	28.65	28.43	-0.01
8	.4187	.5813	.0000	.0000	28.07	28.07	-0.23
9	.4067	.4687	.0111	.1135	29.89	29.74	+0.21
10	.3866	.4253	.0161	.1720	30.80	30.59	+0.46
11	.3684	.3967	.0216	.2133	30.82	30.53	+0.03
12	.3506	.3311	.0287	.2896	31.55	31.17	-0.13
1400 °C							
1	.1191	.7394	.0343	.1072	28.30	27.84	+0.22
2	.1540	.6635	.0320	.1504	28.97	28.54	+0.15
3	.2092	.5775	.0325	.1807	29.24	28.81	-0.15
4	.2437	.5313	.0291	.1959	29.43	29.04	-0.33
5	.2758	.5505	.0210	.1527	29.23	28.95	-0.12
6	.2945	.5830	.0151	.1074	28.77	28.57	-0.08
7	.3228	.5963	.0118	.0691	28.44	28.28	-0.01
8	.4187	.5813	.0000	.0000	27.71	27.71	-0.21
9	.4079	.4701	.0052	.1168	29.67	29.60	+0.22
10	.3879	.4267	.0096	.1758	30.58	30.45	+0.42
11	.3706	.3991	.0096	.2207	30.65	30.52	-0.09
12	.3524	.3332	.0184	.2960	31.60	31.36	-0.02
1300 °C							
1	.1192	.7398	.0332	.1078	28.13	27.70	+0.19
2	.1549	.6673	.0208	.1570	29.02	28.75	+0.14
3	.2105	.5811	.0204	.1880	29.33	29.06	-0.13
4	.2449	.5341	.0188	.2022	29.42	29.18	-0.34
5	.2771	.5531	.0116	.1582	29.23	29.08	-0.08
6	.2953	.5847	.0094	.1106	28.62	28.50	-0.09
7	.3235	.5975	.0078	.0712	28.23	28.20	+0.06
8	.4187	.5813	.0000	.0000	27.34	27.34	-0.22
9	.4085	.4708	.0021	.1185	29.41	29.38	+0.23
10	.3887	.4276	.0053	.1783	30.33	30.22	+0.35
11	.3715	.4000	.0051	.2235	30.35	30.28	-0.20
12	.3537	.3341	.0110	.3012	31.59	31.45	+0.07

X is mole fraction.

V\* = V - X(FeO)V(FeO), see text for discussion of V(FeO).

Table 4. Partial Molar Volumes.

Temperature	V(Na <sub>2</sub> O)	V(Fe <sub>2</sub> O <sub>3</sub> )	V(SiO <sub>2</sub> )
1500 <sup>1</sup>	30.28 (0.58)	40.71 (0.90)	26.86 (0.31)
1400 <sup>1</sup>	29.64 (0.53)	40.69 (0.80)	26.68 (0.28)
1300 <sup>1</sup>	28.90 (0.51)	40.74 (0.77)	26.59 (0.28)
1500 <sup>2</sup>	30.64 (0.71)	40.46 (1.16)	26.67 (0.37)
1400 <sup>2</sup>	29.66 (0.56)	40.67 (0.81)	26.67 (0.29)
1300 <sup>2</sup>	28.90 (0.52)	40.77 (0.77)	26.55 (0.28)

(numbers in brackets represent 1 std. dev.)

<sup>1</sup> ferric/ferrous data from dip quench samples obtained during densitometry.

<sup>2</sup> ferric/ferrous data from drop quench experiments, except for NFS 1 (see text for discussion of this sample).

### Linear fits

The results of the linear regressions at 1300, 1400 and 1500°C are presented in Tables 3 and 4. For comparison, inclusion of the data of BOCKRIS *et al.* (1956) was considered justifiable on the basis of Fig. 4 and the results of a 1400°C linear fit to the combined data set is given in line 2 of Table 5. The values of the partial molar volumes derived from the inclusion of BOCKRIS *et al.* (1956) data do not change within 1 standard deviation.

In Table 4 comparison is made of the calculated partial molar volumes for linear fits using the dip quench redox data and using the drop quench redox data. There are no significant differences.

The quality of fit is indicated by the tabulation of residuals in Table 3 and the square root of the mean of squared residuals or "root mean squared deviation" (RMSD) given in Table 5 as percent of the fitted volume. The best estimate of total uncertainty in our density determinations (including contributions from experimental and analytical accuracy) is 0.55%, as noted above. The linear regressions of Table 4 do not reproduce the density data to within our best estimate of the error of these determinations. Despite this observation, and in the event that our estimation of experimental errors is low, several aspects of the linear regression data are worth noting. The values of the partial molar volumes of Na<sub>2</sub>O and SiO<sub>2</sub> from the 1400°C regression are comparable to those obtained from the linear regressions of STEIN *et al.* (1986) to their density data on melts in the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system at 29.64 ± 0.53 cm<sup>3</sup>/mole and 26.68 ± 0.28 cm<sup>3</sup>/mole *versus*

Table 5. Comparison of various fits at 1400 °C.

V(Na <sub>2</sub> O)	V(Fe <sub>2</sub> O <sub>3</sub> )	V(SiO <sub>2</sub> )	V(excess)	RMSD
(linear)				
29.64 (0.53)	40.69 (0.80)	26.68 (0.28)	-	0.71
29.05 (0.15)	41.34 (0.34)	26.78 (0.10)	-	0.83*
(NaFe)				
27.15 (1.21)	31.59 (4.17)	28.17 (0.71)	29.65 (13.42)	0.56
28.90 (0.16)	38.80 (1.22)	26.89 (0.11)	8.20 (3.78)	0.76*
(NaSi)				
37.49 (2.40)	36.59 (1.36)	28.64 (0.62)	-18.28 (5.52)	0.46
30.54 (0.72)	40.74 (0.43)	27.18 (0.21)	-3.81 (1.80)	0.76*
(FeSi)				
29.70 (1.06)	40.40 (4.22)	26.62 (0.83)	0.73 (10.3)	0.70
29.02 (0.17)	41.93 (1.34)	26.81 (0.12)	-1.29 (2.84)	0.83*
(Na ex.)				
29.67 (0.54)	35.16 (0.38)	26.66 (0.29)	-	0.72

\* fit includes the Na<sub>2</sub>O-SiO<sub>2</sub> data of Bockris *et al.* (1956) (numbers in brackets represent 1 std. dev.).

28.55 ± 0.17 cm<sup>3</sup>/mole and 27.08 ± 0.05 cm<sup>3</sup>/mole. The inclusion of the data for the 16 Na<sub>2</sub>O-SiO<sub>2</sub> melt compositions of BOCKRIS *et al.* (1956) in both regressions results in a convergence of the partial molar volumes of Na<sub>2</sub>O and SiO<sub>2</sub> to 28.92 ± 0.06 cm<sup>3</sup>/mole and 26.84 ± 0.05 cm<sup>3</sup>/mole (STEIN *et al.*, 1986) versus 29.05 ± 0.15 cm<sup>3</sup>/mole and 26.78 ± 0.10 cm<sup>3</sup>/mole (this study) for Na<sub>2</sub>O and SiO<sub>2</sub>, respectively.

The partial molar volume of Fe<sub>2</sub>O<sub>3</sub> (40.69 ± 0.80 cm<sup>3</sup>/mole) obtained from the linear fit of our data at 1400°C is comparable to that reported by BOTTINGA *et al.* (1983) from the study of SHIRAISHI *et al.* (1978) (40.13 ± 0.31 cm<sup>3</sup>/mole) in the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. In contrast, the partial molar volumes of Fe<sub>2</sub>O<sub>3</sub> derived by BOTTINGA *et al.* (1983) from the data reported by HENDERSON (1964) for CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts and the value quoted by MO *et al.* (1982) for multicomponent melts are significantly different at 38.55 ± 0.76 cm<sup>3</sup>/mole and 43.89 ± 1.23 cm<sup>3</sup>/mole, respectively.

Comparison of the partial molar volumes of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in silicate melts with the crystalline volumes of pure Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> (MO *et al.*, 1982; LANGE and CARMICHAEL, 1987) has been interpreted to indicate that the larger partial molar volumes of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in silicate melts compared with the pure crystalline oxides is indicative of tetrahedral coordination of Al and Fe<sup>3+</sup> in silicate melts. The resulting observation, that tetrahedral coordination results in larger molar volumes for Al and Fe<sup>3+</sup>, and the smaller partial molar volume of Fe<sub>2</sub>O<sub>3</sub> derived by BOTTINGA *et al.* (1983) from the data of HENDERSON (1964) in melts in the CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system is consistent with a portion of the Fe<sub>2</sub>O<sub>3</sub> in melts in the CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system being in higher coordination. This possibility is currently under investigation by the present authors.

Unfortunately, the density study of HENDERSON (1964) utilized the less precise, maximum bubble pressure method (see discussion by LANGE and CARMICHAEL, 1987) and the compilation by MO *et al.* (1982) included data obtained by this method, thus the above comparisons are weakened accordingly.

The recent densitometry study of LANGE and CARMICHAEL (1987) has utilized the dip sampling technique (*e.g.*, DINGWELL and VIRGO, 1987, 1988, and this study) resulting in the conclusion (LANGE and CARMICHAEL, 1987) that MO *et al.*'s (1982) redox data are suspect. More importantly, when LANGE and CARMICHAEL (1987) rejected what they determined to be low quality data in their linear fit to a multicomponent data set, including their four new determinations on Fe-bearing melts and the eight Fe-bearing compositions of MO *et al.* (1982), the value of the partial molar volume of Fe<sub>2</sub>O<sub>3</sub> quoted for 1400°C was reduced to 42.13 ± 0.28 cm<sup>3</sup>/mole from the previous value of MO *et al.* (1982) of 43.89 ± 1.23 cm<sup>3</sup>/mole, in closer agreement with the value determined in this study.

#### Nonlinear fits

In order to assess further the validity of using a linear equation to fit the volume data, we regressed the same data using an equation of the form:

$$V = \sum_{i=1}^n X_i V_i + X_j X_k V_{jk} \quad (3)$$

where  $X_j$  and  $X_k$  are the mole fractions of oxide components  $j$  and  $k$  ( $j, k = \text{SiO}_2, \text{Na}_2\text{O}, \text{Fe}_2\text{O}_3$ ), and  $V_{jk}$  is the excess volume term between  $j$  and  $k$ . The results of these nonlinear fits (with and without the BOCKRIS *et al.*, 1956, data) are presented in lines 3 to 8 of Table 5. All fits involving excess products resulted in lower values of RMSD.

The fits involving an FeSi product as the excess term result in excess terms with standard deviations greater than the excess terms. Any excess term that has a standard deviation large enough to allow a positive or negative value is clearly not useful and thus the FeSi excess fits (lines 7 and 8, Table 5) may be discarded.

The fits involving an NaSi product as the excess term are more interesting. Firstly, as described by BOTTINGA *et al.* (1983) (and, indeed by BOCKRIS *et al.*, 1956), there is a trend of negative volumes of mixing in the data of BOCKRIS *et al.* (1956) for melts on the Na<sub>2</sub>O-SiO<sub>2</sub> join. If we accept the error estimate of BOCKRIS *et al.* (1956) for their Na<sub>2</sub>O-SiO<sub>2</sub> data (ave. error = 0.28%) and perform a linear fit to these data ( $V(\text{Na}_2\text{O}) = 30.21 \pm 0.27$  cm<sup>3</sup>/mole,  $V(\text{SiO}_2) = 26.82 \pm 0.06$  cm<sup>3</sup>/mole), the resulting RMSD is slightly larger than the estimated error at 0.31%. A nonlinear fit employing a NaSi product as the excess term ( $V(\text{Na}_2\text{O}) = 30.21 \pm 0.27$  cm<sup>3</sup>/mole,  $V(\text{SiO}_2) = 27.15 \pm 0.80$  cm<sup>3</sup>/mole,  $V(\text{excess}) = -3.24 \pm 0.68$  cm<sup>3</sup>/mole) results in a decrease in the RMSD to 0.19%, within the estimated errors. If we fit a NaSi excess term to our data the RMSD is reduced to 0.46 and thus the calculated volumes reproduce the experimental volumes within the estimated errors of determination (0.55%). The excess term is negative and thus the partial molar volumes of Na<sub>2</sub>O and SiO<sub>2</sub> are increased. The partial molar volume of Fe<sub>2</sub>O<sub>3</sub> is reduced to 36.59 ± 1.36 cm<sup>3</sup>/mole. The partial molar volumes of Na<sub>2</sub>O (37.49 ± 2.40 cm<sup>3</sup>/mole) and SiO<sub>2</sub> (28.64 ± 0.62 cm<sup>3</sup>/mole) are inconsistent with values derived from the linear fits to the data of STEIN *et al.* (1986) and this study and with recommended values from multicomponent linear fitting schemes for aluminum-free (29.03 cm<sup>3</sup>/mole (Na<sub>2</sub>O) and 26.75 cm<sup>3</sup>/mole (SiO<sub>2</sub>); BOTTINGA *et al.*, 1983, Table 4) or aluminum-bearing (28.78 ± 0.10 cm<sup>3</sup>/mole (Na<sub>2</sub>O) and 29.61 ± 0.06 cm<sup>3</sup>/mole (SiO<sub>2</sub>); LANGE and CARMICHAEL, 1987) silicate melts.

As noted above however, the Na<sub>2</sub>O-SiO<sub>2</sub> density data of BOCKRIS *et al.* (1956) show volume deviations from ideal mixing which are generally disregarded by workers who develop linear multicomponent models from their and other's data. In the study of BOCKRIS *et al.* (1956) the partial molar volume of SiO<sub>2</sub> obtained by the graphical method of intercepts varies with composition and is given for pure SiO<sub>2</sub> (at 1400°C) as 27.30 ± 0.03 cm<sup>3</sup>/mole. This value is in agreement with the data of BACON *et al.* (1960) whose higher temperature study on pure SiO<sub>2</sub> illustrated a positive temperature dependence of volume that extrapolates to a 1400°C volume of 27.05 cm<sup>3</sup>/mole. These values are similar to those obtained in the combined (BOCKRIS *et al.*, 1956, and this study) NaSi excess term fit.

Finally, with regard to a NaSi excess term we would add that a nonlinear fit involving a negative CaSi excess term was determined to be the best description of the recent density determinations of LANGE and CARMICHAEL (1987) in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. In contrast, the best Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-

SiO<sub>2</sub> melt density data available, describe a linear variation with composition (STEIN *et al.*, 1986). If we suppose for the moment that volume variations should be similar in form (linear or nonlinear) for all "ternary" aluminosilicate and ferrosilicate systems then we have an apparent discrepancy between the nonlinear description of calcium aluminosilicate and sodium ferrosilicate volume data and the linear description of the sodium aluminosilicate volume data. In view of the facts that 1) the nonlinearity in the Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system is at the limit of statistical detection, 2) BOCKRIS *et al.* (1956) argue for nonlinear behavior in the Na<sub>2</sub>O-SiO<sub>2</sub> system, and 3) the compositional ranges of data for the nonlinear data sets (CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) are much larger than that experimentally accessible in the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, it is tempting to speculate that the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system may be nonlinear with respect to volume.

Nonlinear fits using a NaFe product term as the excess term (lines 3 and 4, Table 5) result in a positive excess term and the quality of fit is comparable to that of the NaSi excess fits discussed above. Statistically, the NaSi and NaFe excess term fits are difficult to choose between but the negative excess term in the data of BOCKRIS *et al.* (1956) leads us to favor the inclusion of this term in the fit to the combined data set.

We performed one more fit to the volume data of this study, predicated on a structural model of the melts. As noted in the introduction, a variety of structural probes have been applied to the study of glasses in the Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system (*e.g.* <sup>57</sup>Fe Mössbauer spectroscopy, DANCKWERTH and VIRGO, 1982; Raman spectroscopy, VIRGO *et al.*, 1982a,b; EXAFS, BROWN *et al.*, 1979; XRD, HENDERSON *et al.*, 1984; Optical absorption and luminescence spectroscopy, FOX *et al.*, 1982; and ESCA, GOLDMAN, 1986). The consensus of these studies is that ferric iron is tetrahedrally coordinated by oxygen atoms, possibly as NaFeO<sub>2</sub>-based tetrahedra. In order to observe the partial molar volumes that would be extracted from our data based on such a model, we recast the compositions into proportions of SiO<sub>2</sub>, NaFeO<sub>2</sub> and Na<sub>2</sub>O. The results of this recast linear regression are included in Table 5 (line 9), illustrating that the partial molar volume of the NaFeO<sub>2</sub> component is 35.16 ± 0.38 cm<sup>3</sup>/mole. This recast fit highlights one point about the role of Na<sub>2</sub>O in these melts. The structural models for the Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems that contain NaFeO<sub>2</sub> and NaAlO<sub>2</sub> components involve two distinct roles for Na<sub>2</sub>O, namely network-modifier and network-stabilizer. Thus, the success of linear fits to the volume data in these two systems (*i.e.*, constant partial molar volumes of Na<sub>2</sub>O in these melts) combined with the above structural models would indicate that the volume of Na<sub>2</sub>O is insensitive to the structural role of this component. It remains to be seen whether the same is true for ferric iron.

#### SUMMARY

This study of melt densities in the Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system is a starting point for the investigation of the partial molar volume of Fe<sub>2</sub>O<sub>3</sub> in well-investigated silicate melt systems, using samples with well-characterized oxidation states. Previous studies of the structure of melts and glasses in this

system have suggested that ferric iron is tetrahedrally-coordinated in these melts. Thus we consider the values of the partial molar volume of Fe<sub>2</sub>O<sub>3</sub> obtained from this study to be the best estimates to date for the volume of tetrahedrally-coordinated ferric iron in silicate melts.

We have provided linear and nonlinear fits to these data and our comparison of the fit errors to our best estimate of experimental uncertainty indicates that a small excess term is required to reproduce these data. The form of the excess term is difficult to constrain but evidence for a negative volume of mixing on the Na<sub>2</sub>O-SiO<sub>2</sub> join leads us to favor a negative NaSi product term to best describe the data in the Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. Excellent agreement between the results of this study and those of BOCKRIS *et al.* (1956) leads us to combine the data sets for the fits. The resulting NaSi excess fit of the combined data set results in the lowest RMSD of all the fits attempted and reasonable values for all the partial molar volumes.

The work forms a useful starting point for a systematic investigation of the hypothesis that the partial molar volume of ferric iron varies with composition. The decision of how best to treat the calculation of the partial molar volume of Fe<sub>2</sub>O<sub>3</sub> and possibly, by analogy, Al<sub>2</sub>O<sub>3</sub> (GHIORSO and CARMICHAEL, 1984) in silicate melts must await the results of further work on compositionally-simple, related systems. Work is in progress towards this goal (DINGWELL and BREARLEY, 1988).

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#### REFERENCES

- BACON J. F., ASAPIS A. A. and WHOLLEY JR. J. W. (1960) Viscosity and density of molten silica and high silica content glasses. *Phys. Chem. Glasses* **1**, 90–98.
- BOCKRIS J. O'M., TOMLINSON J. W. and WHITE J. L. (1956) The structure of the liquid silicates: partial molar volumes and expansivities. *Faraday Soc. Trans.* **52**, 299–310.
- BOTTINGA Y. and WEILL D. (1970) Densities of liquid silicate systems calculated from partial molar volumes of oxide components. *Amer. J. Sci.* **269**, 169–182.
- BOTTINGA Y., WEILL D. and RICHEL P. (1982) Density calculations for silicate liquids. I. Revised method for aluminosilicate compositions. *Geochim. Cosmochim. Acta* **46**, 909–919.
- BOTTINGA Y., RICHEL P. and WEILL D. (1983) Calculation of the density and thermal expansion coefficient of silicate liquids. *Bull. Mineral.* **106**, 129–138.
- BOTTINGA Y., WEILL D. and RICHEL P. (1984) Density calculations for silicate liquids: Reply to a critical comment by Ghiorso and Carmichael. *Geochim. Cosmochim. Acta* **48**, 409–414.
- BOWEN N. L., SCHAIRER J. F. and WILLEMS H. W. V. (1930) The ternary system: Na<sub>2</sub>SiO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *Amer. J. Sci.* **28**, 405–455.
- BROWN G., KEEFER K. D. and FENN P. M. (1979) Extended X-ray absorption fine structure (EXAFS) study of iron-bearing silicate glasses: iron coordination environment and oxidation state. *Geol. Soc. Amer. Abstr. Prog.* **11**, 373.



- CAMPBELL I. H. and TURNER J. S. (1986) The role of convection in the formation of platinum and chromitite deposits in layered intrusions. In *MAC Short Course in Silicate Melts* (ed. C. M. SCARFE), pp. 236–278. Mineral. Assoc. of Canada.
- CANIL D. and MUEHLENBACHS K. (1987) Self-diffusion of oxygen in an Fe-rich basalt melt. *Geol. Soc. Amer. Abstr. Prog.* **19**, 610.
- CARMICHAEL I. S. E. and GHIORSO M. S. (1986) Oxidation-reduction relations in basic magma: A case for homogeneous equilibria. *Earth Planet. Sci. Lett.* **78**, 200–210.
- DANCKWERTH P. A. and VIRGO D. (1982) Structural state of iron in the system Na<sub>2</sub>O-SiO<sub>2</sub>-Fe-O. *Carnegie Inst. Wash. Yearb.* **81**, 340–342.
- DANEK V., LICKO T. and PANEK Z. (1985) Viscosity of melts in the system CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *Silikaty* **29**, 291–299.
- DICKENSON M. P. and HESS P. C. (1981) Redox equilibria and the structural role of iron in aluminosilicate melts. *Contrib. Mineral. Petrol.* **78**, 352–358.
- DICKENSON M. P. and HESS P. C. (1986a) The structural role and homogeneous redox equilibria of iron in peraluminous, metaluminous and peralkaline silicate melts. *Contrib. Mineral. Petrol.* **92**, 207–217.
- DICKENSON M. P. and HESS P. C. (1986b) The structural role of Fe<sup>3+</sup>, Ga<sup>3+</sup>, Al<sup>3+</sup> and homogeneous iron redox equilibria in K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-FeO melts. *J. Non-Cryst. Sol.* **86**, 303–310.
- DINGWELL D. B. and BREARLEY M. (1987) Melt densities in the Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system and the partial molar volume of tetrahedrally-coordinated ferric iron in silicate melts. *Geol. Soc. Amer. Abstr. Prog.* **19**, 643.
- DINGWELL D. B. and BREARLEY M. (1988) A test of the composition-dependence of the partial molar volume of ferric iron in silicate melts. *2nd Intl. Symp. Exptl. Mineral., Petrol. and Geochem., Terra Cognita* **8**, 61.
- DINGWELL D. B. and VIRGO D. (1987) The effect of oxidation state on the viscosity of melts in the system Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *Geochim. Cosmochim. Acta* **51**, 195–205.
- DINGWELL D. B. and VIRGO D. (1988) Viscosities of melts in the Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system and a discussion of factors controlling the relative viscosities of fully polymerized silicate melts. *Geochim. Cosmochim. Acta* **52**, 395–403.
- EDWARDS J. W., SPEISER R. and JOHNSON L. (1951) High temperature structure and thermal expansion of some metals as determined by X-ray diffraction. I. Platinum, tantalum, niobium and molybdenum. *J. Appl. Phys.* **22**, 424–428.
- FOX K. E., FURUKAWA T. and WHITE W. B. (1982) Transition metal ions in silicate melts. Part 2. Iron in sodium silicate glasses. *Phys. Chem. Glasses* **23**, 169–178.
- GHIORSO M. S. and CARMICHAEL I. S. E. (1984) Comment on "Density calculations for silicate liquids. I. Revised method for aluminosilicate compositions" by Bottinga, Weill and Richet. *Geochim. Cosmochim. Acta* **48**, 401–408.
- GOLDMAN D. S. (1986) Evaluation of the ratios of bridging to non-bridging oxygens in simple silicate glasses by electron spectroscopy for chemical analysis. *Phys. Chem. Glasses* **27**, 128–133.
- HENDERSON G. S., FLEET M. S. and BANCROFT G. M. (1984) An X-ray scattering study of vitreous KFeSi<sub>3</sub>O<sub>8</sub> and NaFeSi<sub>3</sub>O<sub>8</sub> and reinvestigation of vitreous silica using quasicrystalline modelling. *J. Non-Cryst. Sol.* **68**, 333–349.
- HENDERSON J. (1964) Density of lime-iron oxide-silicate melts. *Trans. Metall. Soc. AIME* **20**, 501–504.
- HERZBERG C. (1987) Magma density at high pressure Part 2: A test of the olivine flotation hypothesis. In *Magmatic Processes: Physicochemical Principles* (ed. B. O. MYSEN), pp. 47–58. *Geochem. Soc. Spec. Publ.* **1**.
- HUPPERT H. E. and SPARKS R. S. J. (1980) The fluid dynamics of a basaltic magma chamber replenished by influx of hot, dense ultrabasic magma. *Contrib. Mineral. Petrol.* **75**, 279–289.
- JANZ G. J. (1980) Molten salts data as reference data for density, surface tension, viscosity and electrical conductance: KNO<sub>3</sub> and NaCl. *J. Phys. Chem. Ref. Data* **9**, 791–829.
- KILINC A., CARMICHAEL I. S. E., RIVERS M. L. and SACK R. O. (1983) The ferric/ferrous ratio of natural silicate liquids equilibrated in air. *Contrib. Mineral. Petrol.* **83**, 136–140.
- KRESS V. C., WILLIAMS Q. and CARMICHAEL I. S. E. (1988) Ultrasonic investigation of melts in the system Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *Geochim. Cosmochim. Acta* **52**, 283–293.
- LANGE R. A. and CARMICHAEL I. S. E. (1987) Densities of K<sub>2</sub>O-Na<sub>2</sub>O-CaO-MgO-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub> liquids: New measurements and derived partial molar properties. *Geochim. Cosmochim. Acta* **51**, 2931–2946.
- LICKO T., DANEK V. and PANEK Z. (1985) Densities of melts in the system CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *Chem. Papers* **39**, 599–605.
- MANGHNANI M. H., SATO H. and RAI C. S. (1986) Ultrasonic velocity and attenuation measurements on basalt melts to 1500°C: Role of composition and structure in the viscoelastic properties. *J. Geophys. Res.* **91**, 9333–9342.
- MO X., CARMICHAEL I. S. E., RIVERS M. and STEBBINS J. (1982) The partial molar volume of Fe<sub>2</sub>O<sub>3</sub> in multicomponent silicate liquids and the pressure dependence of oxygen fugacity in magmas. *Mineral. Mag.* **45**, 237–245.
- MYSEN B. O. (1988) Relation between structure, redox equilibria of iron and properties of magmatic liquids. In *Advances in Physical Geochemistry* (eds. I. KUSHIRO and L. PERCHUK), in press.
- MYSEN B. O., VIRGO D., NEUMANN E. and SEIFERT F. A. (1985) Redox equilibria and the structural states of ferric and ferrous iron in melts in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Fe-O: Relationships between redox equilibria, melt structure and liquidus phase equilibria. *Amer. Mineral.* **70**, 317–331.
- RIVERS M. L. and CARMICHAEL I. S. E. (1987) Ultrasonic studies of silicate melts. *J. Geophys. Res.* **92**, 9247–9270.
- SACK R. O., CARMICHAEL I. S. E., RIVERS M. L. and GHIORSO M. S. (1980) Ferric-ferrous equilibria in natural silicate liquids at 1 bar. *Contrib. Mineral. Petrol.* **75**, 369–376.
- SEKI K. and OETERS F. (1984) Viscosity measurements on liquid slags in the system CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *Trans. Iron Steel Inst. Jap.* **24**, 445–454.
- SHIMIZU N. and KUSHIRO I. (1984) Diffusivity of oxygen in jadeite and diopside melts at high pressures. *Geochim. Cosmochim. Acta* **48**, 1295–1304.
- SHIRAIISHI Y., IKEDA K., TAMURA A. and SAITO T. (1978) On the viscosity and density of the molten FeO-SiO<sub>2</sub> system. *Trans. Jap. Inst. Metal.* **19**, 264–274.
- STEIN D. J., STEBBINS J. F. and CARMICHAEL I. S. E. (1986) Density of molten sodium aluminosilicates. *J. Amer. Ceram. Soc.* **69**, 396–399.
- TOGURI J., KAIURA G. H. and MARCHANT G. (1976) The viscosity of molten FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. In *Extraction Metallurgy of Copper. I. Physical Chemistry of Copper Smelting*, pp. 259–273. Metall. Soc. of AIME, New York.
- VIRGO D. and MYSEN B. O. (1985) The structural state of iron in oxidized versus reduced glasses at 1 atm: a <sup>57</sup>Fe Mössbauer study. *Phys. Chem. Mineral.* **12**, 65–76.
- VIRGO D., MYSEN B. O., DANCKWERTH P. and SEIFERT F. (1982a) The anionic structure of 1-atm melts in the system SiO<sub>2</sub>-NaFeO<sub>2</sub>. *Carnegie Inst. Wash. Yearb.* **81**, 347–349.
- VIRGO D., MYSEN B. O., DANCKWERTH P. and SEIFERT F. (1982b) Speciation of Fe<sup>3+</sup> in 1-atm Na<sub>2</sub>O-SiO<sub>2</sub>-Fe-O melts. *Carnegie Inst. Wash. Yearb.* **81**, 349–353.
- WASEDA Y., HIRATA K. and OHTANI M. (1975) High temperature thermal expansion of platinum, tantalum, molybdenum and tungsten measured by X-ray diffraction. *High-Temp. High Pressures* **7**, 221–226.
- WILSON A. D. (1960) The micro-determination of ferrous iron in silicate minerals by a volumetric and a colorimetric method. *Analyst* **85**, 823–827.