Redox viscometry of some Fe-bearing silicate melts

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Abstract

The dependence of shear viscosity on the oxidation state of six ferrosilicate melts has been measured using the concentric cylinder method and a gas mixing furnace. The measurements were performed under air, CO_2, and CO_2-CO mixtures at 1 atm and in a temperature range of 1345 to 1470 °C. The experimental procedure involved a continuous measurement of viscosity during stepwise reduction of the melts. Melt chemistry was controlled by dip sampling the liquids at each oxidation state. The resulting glasses were analyzed by electron microprobe, a volumetric FeO titration, and ^{57}Fe Mössbauer spectroscopy. The electron microprobe data indicate Fe loss for some of the most reduced samples. The wet chemical (+ microprobe) and spectroscopic determinations of these Fe-rich samples yield oxidation states that are in excellent agreement.

The viscosity of all melts investigated herein decreases with melt reduction. The viscosity decrease is, in general, a nonlinear function of oxidation state expressed as Fe^{2+}/Fe_{tot}.

Introduction

Most of the physical properties of ferrosilicates depend significantly on oxidation state. In addition, the redox dependence of some properties such as density (Dingwell et al., 1988; Hara et al., 1988) and viscosity (Montenero et al., 1986; Dingwell and Virgo, 1988) is nonlinear. Correct structural inferences from the physical properties of ferrosilicate melts thus require close control of the effects of oxidation state. This study extends the observations of Dingwell and Virgo (1988) that viscosity follows a nonlinear decrease with reduction of Fe in ferrosilicate melts.

Method

The starting materials for these experiments were the products of an earlier study: glasses KFS2 ($KFeSi_2O_x$), BFS2 ($Ba_{0.5}FeSi_2O_x$), RFS2 ($RbFeSi_2O_x$), and SFS2 ($Sr_{0.5}FeSi_2O_x$) of Dingwell (1989). Analyses of the starting glasses are provided in Table 2 of Dingwell (1989). These glasses had been obtained by pouring the contents of $Pt_{80}Rh_{20}$ crucibles onto a stainless steel plate for cooling. In the present study, chips of these glasses were melted stepwise into $Pt_{80}Rh_{20}$ viscometry crucibles (2.5 cm inner diameter, 5 cm height, 2 mm wall thickness) in a $MoSi_2$ box furnace at 1500 °C. The melted samples were then transferred to a vertical tube furnace for the viscosity determinations under varying O_2 pressure.

The experimental procedure used is similar to that described by Dingwell and Virgo (1987). The samples were first equilibrated in air at temperature. The temperatures were chosen to lie above the liquidus and to yield viscosities in the range of 10–100 dPaS. Viscosities greater than this range lead to excessively long redox equilibration times, and viscosities lower than this range are difficult to quench without crystallization.

Viscosity was measured using the concentric cylinder method. The spindle is that described by Dingwell (1989). The viscometer head is a Brookfield model RVTD with a full range torque of 7.2×10^{-2} N-m. This combination of head, spindle, and crucible has been calibrated using standard glasses of known viscosity (National Bureau of Standards SRM-711 and Deutsche Glastechnische Gesellschaft DGG-1). The viscosities have a precision of $\pm2.5\%$ and an accuracy including the standard glass precision equal to $\pm5\%$. In the present experiments, the viscosity spindle was turned continuously in the melt to enhance the equilibration rate. The viscosity was thus monitored continuously. The melt was reduced by flowing CO_2 and then successively reducing mixtures of CO_2-CO through the alumina muffle tube. Gas flow rates were electronically controlled using Tylan mass flow controllers. The composition and oxidation state of the melt was monitored by obtaining a melt sample after each redox equilibration step. The melts were sampled by dipping a Pt wire loop into the sample and drawing out a drop of liquid, which was then plunged into H_2O for quenching. For melts in this viscosity range, this "dip" sampling technique yields oxidation state data indistinguishable from that obtained by the more conventional drop quench method (Dingwell and Virgo, 1987). The samples obtained by this method were powdered to obtain ^{57}Fe Mössbauer spectra. The results of the ^{57}Fe Mössbauer spectroscopy are presented in Table 1. The same powders were analyzed using the wet chemical volumetric method of Wilson (1960), and a fraction of the powders were mounted for electron microprobe analysis. The results of the wet chemical determinations of Fe^{2+} are presented in Table 2, and the electron microprobe analyses are presented in Table 3. The oxidation states of the glasses determined from wet chemical and ^{57}Fe Mössbauer analyses

TABLE 1. The ^{57}Fe Mössbauer spectroscopic data

Sample	IS (3)	QS (3)	IS (2)	QS (2)	Fe^{3+}/Fe_{tot}
SFS2-1	0.33	1.06	0.90	2.05	0.889
SFS2-2	0.32	1.07	0.90	2.11	0.755
SFS2-3	0.33	1.04	0.95	2.15	0.724
SFS2-4	0.31	1.09	1.03	1.91	0.604
BFS2-1	0.27	1.06	0.86	2.08	0.855
BFS2-2	0.33	0.95	0.96	2.16	0.817
BFS2-3	0.37	0.88	0.99	2.02	0.742
BFS2-4	0.38	0.86	0.90	2.11	0.704
RFS2-1	0.22	0.78	0.88	1.81	0.952
RFS2-2	0.24	0.73	0.85	1.98	0.847
RFS2-3	0.33	0.55	0.85	2.02	0.559
RFS2-4	0.47	0.25	0.90	1.94	0.350
KFS2-1	0.23	0.77	0.83	2.04	0.941
KFS2-2	0.23	0.76	0.89	1.92	0.858
KFS2-3	0.49	0.24	0.89	1.94	0.267
KFS2-4	0.50	0.21	0.92	1.92	0.230

Note: IS is isomer shift in mm/s and QS is quadrupole splitting in mm/s. The numbers (2) and (3) refer to Fe^{2+} and Fe^{3+}, respectively.

TABLE 3. Electron microprobe analyses (wt%)

Sample	X_2O, XO $X =$	FeO*	SiO_2	Total**
SFS-1 (Sr)	20.6(1)	30.1(7)	46.2(9)	99.6
SFS-2	20.6(1)	30.1(4)	46.5(2)	99.5
SFS-3	20.5(1)	30.1(1)	46.8(2)	99.6
SFS-4	20.6(1)	30.2(4)	46.7(4)	99.6
BFS-1 (Ba)	25.4(1)	29.7(3)	43.3(2)	98.4
BFS-2	26.0(3)	29.8(1)	42.6(2)	98.4
BFS-3	25.9(2)	29.7(2)	42.4(3)	98.0
BFS-4	26.1(7)	29.8(1)	42.6(2)	98.9
RFS-1 (Rb)	30.3(1)	25.3(2)	40.0(1)	98.1
RFS-2	30.3(9)	25.2(1)	40.8(9)	98.5
RFS-3	28.6(8)	24.5(3)	44.2(7)	97.3
RFS-4	30.7(2)	24.8(6)	41.7(8)	97.2
KFS-1 (K)	18.4(2)	28.7(4)	47.8(5)	97.8
KFS-2	18.2(1)	29.1(2)	48.5(1)	98.4
KFS-3	18.2(1)	25.2(8)	54.4(9)	98.4
KFS-4	18.4(2)	26.3(8)	53.1(6)	98.5

Note: Numbers in parentheses are standard deviation from five analyses.
* Total Fe as FeO.
** Totals corrected for actual oxidation state using wet chemical FeO data.

are compared in Figure 1. The agreement between the methods is similar to that observed in earlier comparisons (Mysen et al., 1985; Joseph et al., 1990). There is no evidence of a bias toward higher Fe^{3+} from the spectroscopic results in these very Fe-rich samples.

RESULTS

The results of the viscosity determinations are presented in Table 4. The relationships of viscosity vs. oxidation state of the four new compositions presented here are similar to those previously observed for $NaFeSi_2O_x$ and $CaFeSi_2O_x$ (Dingwell and Virgo, 1987, 1988). All these data are summarized in Figure 2. It can be seen that the viscosity of all the investigated compositions decreases with melt reduction and that this decrease is demonstrably nonlinear for the Ca-, Na-, K-, and Rb-bearing liquids. The data for the Ba- and Sr-bearing liquids are not sufficient to distinguish such nonlinearity, but the decrease of viscosity with melt reduction appears smaller for the Ba- and Sr-bearing melts than for the alkali ferrosilicates.

Viscosity-temperature relationships of Fe-bearing melts

TABLE 2. Wet chemical FeO determinations (wt%)

Sample	FeO	Fe^{2+}/Fe_{tot}
SFS2-1	6.19(3)	0.188
SFS2-2	8.95(2)	0.220
SFS2-3	9.9(2)	0.254
SFS2-4	13.90(4)	0.414
BFS2-1	4.21(2)	0.141
BFS2-2	5.17(4)	0.173
BFS2-3	8.31(3)	0.279
BFS2-4	9.88(3)	0.332
RFS2-1	3.06(2)	0.121
RFS2-2	5.61(3)	0.223
RFS2-3	11.75(7)	0.47
RFS2-4	15.1(2)	0.624
KFS2-1	2.94(1)	0.103
KFS2-2	6.0(2)	0.206
KFS2-3	18.69(3)	0.743
KFS2-4	20.4(1)	0.774

Note: Numbers in parentheses are standard deviation (in the last significant digit).

of constant oxidation state have been measured by several authors (Urbain et al., 1982; Klein et al., 1983; Montenero et al., 1986; Joseph et al., 1990). These data indicate that the temperature dependence of the melt viscosity is not strongly affected by the oxidation state. This implies that the relationships of viscosity vs. oxidation state in Figure 2 can be taken, as a first approximation, to be independent of temperature.

At least two studies have reported increasing viscosity with melt reduction (Toguri et al., 1976; Seki and Oeters, 1984). Toguri et al. (1976) investigated Fe-Si-O melts of very low Si content, and Seki and Oeters (1984) investigated Ca-Fe-Si-O melts. The melt compositions of Toguri et al. (1976) are so unlike any of the silicate melts investigated here that direct comparison is not possible. It remains possible that the structural roles of Fe^{3+} or Fe^{2+} are different in extremely Fe-rich and silica-poor melts

$$y = 1.06(5)x - 0.05(4)$$
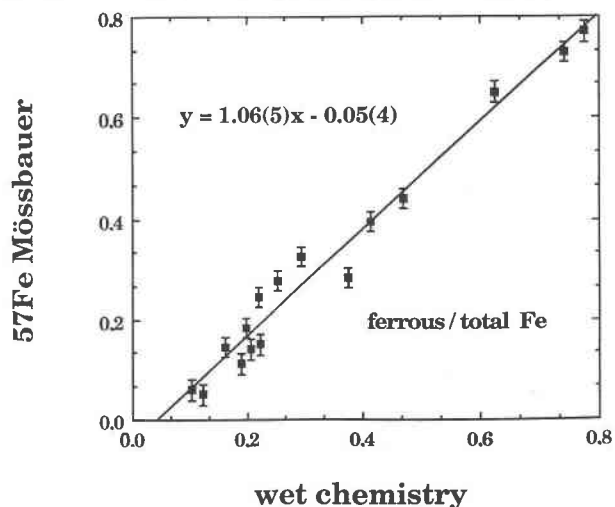
ferrous / total Fe

57Fe Mössbauer

wet chemistry

Fig. 1. Comparison of ^{57}Fe Mössbauer and wet chemical plus electron microprobe determinations of the oxidation state of Fe-bearing silicate glasses.

TABLE 4. Viscosity data

Sample/temperature	$\log_{10}\eta$ (dPaS)
SFS2-1 1350 °C	1.22
SFS2-2	1.14
SFS2-3	1.13
SFS2-4	1.07
BFS2-1 1345 °C	1.45
BFS2-2	1.42
BFS2-3	1.35
BFS2-4	1.33
RFS2-1 1470 °C	1.94
RFS2-2	1.80
RFS2-3	1.45
RFS2-4	1.33
KFS2-1 1380 °C	1.99
KFS2-2	1.83
KFS2-3	1.38
KFS2-4	1.39

and that the relationships of viscosity vs. oxidation state observed by Toguri et al. (1976) contrast with those observed for more SiO_2-rich melts (this study; Cukierman and Uhlmann, 1974; Klein et al., 1983; Montenero et al., 1986; Joseph et al., 1990) for those reasons. The compositions investigated by Seki and Oeters (1984) are not so unlike those investigated in this study, and so composition dependence of the redox effect is an unlikely explanation of the contrasting trends observed. In this respect, it is worth noting that the most reduced compositions of Dingwell and Virgo (1988) experienced the loss of a few percent of Fe, presumably to the crucible, which was fully reversible under the temperature and duration of that study. Such Fe loss is the probable cause of the viscosity rise under very reducing conditions observed by Dingwell and Virgo (1988). The small effect
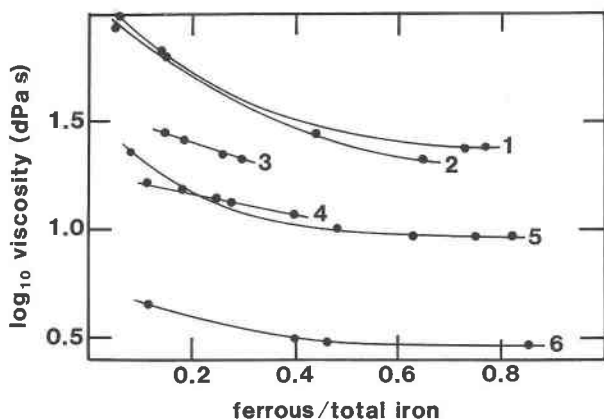

Fig. 2. The oxidation state dependence of shear viscosity for several Fe-bearing silicate melts. (1 = $KFeSi_2O_x$ at 1380 °C; 2 = $RbFeSi_2O_x$ at 1470 °C; 3 = $Ba_{0.5}FeSi_2O_x$ at 1345 °C; 4 = $Sr_{0.5}FeSi_2O_x$ at 1350 °C; 5 = $NaFeSi_2O_x$ at 1430 °C (data from Dingwell and Virgo, 1987); and 6 = $CaFeSi_2O_x$ at 1400 °C (data from Dingwell and Virgo, 1988).

observed by Seki and Oeters (1984) could have a similar origin.

CONCLUSION

The viscosities of alkali- and alkaline-earth ferrosilicates decrease with the reduction of Fe. The viscosity decrease is strong at oxidizing conditions but diminishes to zero with increasing reduction of the melts.

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