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Shear viscosities of ferrosilicate liquids

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ABSTRACT

The shear viscosities of liquids along the alkali and alkaline-earth silicate-ferrite joins, SiO_2-$X^{n+}Fe_nO_{2n-y}$ (where X represents Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba), have been measured at 1 atm and temperatures of 1100 to 1650 °C by using the concentric-cylinder method. All liquids exhibit Newtonian behavior in the range of shear rates investigated, and their viscosity-temperature relationships may be expressed using Arrhenian equations. At a constant temperature, the viscosity-composition relationships of the silicate-ferrite joins describe a set of subparallel curves. At constant SiO_2 content, the liquid viscosities decrease in the sequence Cs > Rb > K > Na > Ba > Sr > Ca > Mg > Li.

The oxidation states of all liquids that could be quenched to glasses were determined by ^{57}Fe Mössbauer spectroscopy. The Fe^{2+} contents of quench glasses increase with increasing temperature and are higher for the Li and alkaline-earth ferrosilicates than for the ferrosilicates with larger-radii alkalis.

The viscosity-composition relationships for these silicate-ferrite joins are qualitatively similar to those of the equivalent silicate-aluminate and silicate-galliate joins, and thus a common structural explanation of the viscosities of all these melts, in terms of relative mean bond strengths, is sufficient to describe most of the observed variation.

INTRODUCTION

The viscosity-temperature relationships of aluminosilicate melts of "tectosilicate" composition (i.e., those compositions corresponding to a calculated NBO/T of 0) have been used as a measure of the relative stability of aluminate tetrahedra in aluminosilicate network structure (e.g., Bottinga and Weill, 1972).

Previous studies of viscosity-temperature relationships for fully polymerized, alkali and alkaline-earth aluminosilicate liquids (i.e., liquids with tectosilicate stoichiometry) define a trend of decreasing viscosity with increasing field strength or decreasing basicity of the network-stabilizing (alkali or alkaline-earth) cation. Thus, the viscosities of such liquids [compared at equal temperature and Al/(Al + Si) content] decrease in the order K > Na > Li and Ba > Sr > Ca > Mg (Urbain et al., 1982; Dingwell, unpublished).

In a recent study of melt viscosities in the Na_2O-FeO-Fe_2O_3-SiO_2 system, Dingwell and Virgo (1988a) observed that a similar relationship between cationic electronegativity and viscosity exists for trivalent cationic substitutions with viscosities decreasing in the order Al > Ga > Fe > B. If such a relationship holds, in general, for tectosilicate melts, then these melts may represent a simplified subset of silicate melts with respect to viscous flow. The stoichiometric constraint of relatively simple structures for such liquids and the existence of other types of thermochemical and physical data on these compositions (Roy and Navrotsky, 1984; Dingwell et al., 1988; Dingwell and Brearley, 1988) provide an opportunity to relate atomistic or microscopic parameters of melt components (e.g., measures of the relative electronegativities of cations) to macroscopic, bulk properties of these liquids (e.g., heats of mixing, densities, and viscosities).

In order to test whether such an electronegativity-viscosity relationship (outlined above) holds for tectosilicate melts, a series of viscosity studies has been initiated for ferrosilicate, galliosilicate, and borosilicate melts. This paper presents the results of viscosity determinations for ferrosilicate melts whose fully oxidized stoichiometry is tectosilicate (assuming a network-forming role for the trivalent cations). Ferrosilicate melts containing Cs, Rb, K, Na, Li, Ba, Sr, Ca, and Mg have been investigated. The data are compared with viscosity data for stoichiometrically equivalent aluminosilicate and galliosilicate melts (related by the exchange operators, $AlFe_{-1}$ and $GaFe_{-1}$). The data are consistent with the trend of increasing cationic electronegativity versus decreasing viscosity.

It is postulated that the influence of the electronegativity of network-stabilizing cations on the mean strength of bonds in the tetrahedral network structure is sufficient to explain the relative viscosities of the aluminosilicate, ferrosilicate, and galliosilicate melts of tectosilicate stoichiometry.

EXPERIMENTAL METHOD

The compositions of this study were chosen to lie along the joins SiO_2-$X^{n+}Fe_nO_{2n}$, where X represents Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba. The (hypothetical) fully oxidized melts along these joins have the same cation stoichiometry as aluminosilicate joins for which viscosity data already exist (i.e., K, Na, Mg, Ca, Sr, and Ba aluminosilicates; Urbain et al., 1982). At high temperature, of course, all the ferrosilicate melts contain significant Fe^{2+}, and the significance of this is discussed below. Where possible, compositions at Si/(Fe + Si) (molar) equal to 0.75 (Cs, Rb, K, Na, Ba, and Li), 0.67 (Cs, Rb, K, Na, Ba, Sr, and Li), and 0.50 (Rb, K, Ba, Sr, and Li) were synthesized to enable direct comparison of viscosities at constant SiO_2 content. The two Ca ferrosilicate melts were chosen to achieve low liquidus temperatures (Phillips and Muan, 1959) in order that a significant temperature range could be accessed for viscosity measurement. The two compositions chosen (33 and 55 mol% SiO_2) are samples CFS4 and CFS5 from the density study of Dingwell and Brearley (1988). Similarly, the single Mg ferrosilicate melt (52 mol% SiO_2) represents the liquidus minimum of the SiO_2-$MgFe_2O_x$ join in equilibrium with air (Muan and Osborn, 1956).

The starting materials for the synthesis of the melts investigated in this study were Li_2CO_3, Na_2CO_3, MgO, SiO_2, K_2CO_3, $CaCO_3$, Fe_2O_3, Rb_2CO_3, $SrCO_3$, Cs_2CO_3, and $BaCO_3$. All materials were dried and stored at 120 °C prior to weighing. Powder mixtures corresponding to a decarbonated weight of 100 g were weighed into a plastic beaker, transferred to a plastic bottle and mixed by agitation for approximately 15 min. Small portions of the mixed powders were added step-wise to a 50-cm^3 Pt crucible and fused directly at 1600 °C for 1–2 h. Most of the molten products were poured from the crucible onto a steel plate for cooling. A few of the more viscous samples were allowed to cool in the crucible and then broken from the crucible with a hammer. Chips of these samples were progressively melted into the viscometry crucibles.

The shear viscosities were measured at 1 atm and temperatures in the range of 1100 to 1650 °C, in air, by using the concentric-cylinder method. This apparatus is similar to that described by Dingwell (1986) with modifications discussed by Dingwell (1989). The furnace is a $MoSi_2$-element box furnace. The viscometer heads are Brookfield models HBTD, RVTD, and LVTD (with full-scale torques of 5.75×10^{-1}, 7.20×10^{-2}, and 6.80×10^{-3} N·m, respectively), and the spindles are identical to those described by Dingwell and Virgo (1988a). The spindles and sample crucibles are fabricated from $Pt_{80}Rh_{20}$. This viscometry installation is capable of measurements from 1 to 10^6 poises, with an accuracy of ±5% at 2σ (Dingwell, 1989).

The rotation rates used vary with the spindle and viscosity of the sample between 0.5 and 100 rpm. In general, the method employed here results in higher shear rates for the determination of lower viscosity data. For any individual determination, a range of about 0.67 orders of magnitude in rotation speed, and therefore shear rate, is accessible within a reasonable error range. No shear-rate dependence of viscosity was observed.

The shear rate corresponding to the onset of non-Newtonian behavior in silicate melts provides a time scale of deformation that is closely related to the structural relaxation time scale of the melt (Dingwell and Webb, 1989). The most probable relaxation time of each silicate melt corresponds to the time scale (inverse of the frequency) of an oxygen jump. The oxygen jump is, in turn, the unit of diffusion and viscous flow in liquid silicates (Dingwell and Webb, 1989). There is a considerable literature dealing with the nature of structural relaxation in liquid silicates and, in particular, with the description of relaxation times in liquids (Wong and Angell, 1976; Brawer, 1985; Scherer, 1986). Dingwell and Webb (1989) have demonstrated that the relaxation time calculated for silicate melts by using the Maxwell relation

$$\tau_s = \eta_s/G_\infty, \tag{1}$$

where τ_s is the shear relaxation time, η_s is the shear viscosity, and G_∞ is the infinite frequency shear modulus, is consistent with relaxation times derived from a number of investigations of microscopic and macroscopic properties of silicate melts. For silicate melts, G_∞ may be estimated at 10 GPa ± 0.5 $\log_{10}$ units (Bansal and Doremus, 1986; Dingwell and Webb, 1989). The calculated relaxation time for the highest viscosities observed in this study is $10^{-5.3}$ s. In comparison, the time scale of the present concentric-cylinder viscometry measurements (the inverse of the shear or strain rate, calculated as $60/(2\pi)$ revolutions per minute) is $10^{-1.0}$ to $10^{1.3}$ s. Thus the observation of Newtonian rheology in this study is consistent with the prediction of relaxed (liquid) behavior at these strain rates.

Measurements were made starting with the highest temperature point and reducing temperature, generally in 25 or 50 °C steps, until crystallization was detected by unstable readings or an instrumental limit was reached. The last measurement of viscosity was always a redetermination of the highest temperature determination to test for experimental drift. No difference was observed between first and last "high-temperature" determinations, indicating that no compositional or instrumental drift occurred during the viscosity determinations.

The oxidation state of the melts was monitored by sampling the melts at each temperature point. A Pt wire loop was dipped into the melt, and a small (50–200 mg, depending on viscosity) sample was extracted and quenched in water. Some samples did not quench to glasses, and the oxidation state of these must be approximated, at best, by making the (quite reasonable) assumption of equilibrium for these very fluid melts and by using composition–oxidation state calculation methods based on data from previous studies of redox equilibria in these and related systems (Thornber et al., 1980; Sack et al., 1980; Kilinc et al., 1983; Mysen, 1989). Glassy "dip"-quenched samples were analyzed for oxidation state using ^{57}Fe Mössbauer spectroscopy. Resonant absorption ^{57}Fe Mössbauer spectra were collected at 25 °C with a 50-mC ^{57}Co/Rh source, on powders contained between sheets of Al foil. The absorber thickness was constrained to yield 5 mg of Fe per square centimeter. Mirror-image spectra were recorded over 512 channels, folded, and analyzed. The spectral data were fitted with the least-squares fitting

Table 1. ^{57}Fe Mössbauer parameters of quenched melts

Sample	Temp. (°C)	Fe³⁺ I.S.	Fe³⁺ Q.S.	Fe²⁺ I.S.	Fe²⁺ Q.S.	Fe^{3+}/Fe_{Total}
RFS1	1450	0.24	0.72	0.78	2.17	0.92
RFS1	1500	0.24	0.73	0.82	2.06	0.92
RFS2	1475	0.23	0.68	0.82	2.19	0.94
RFS2	1525	0.24	0.72	0.80	2.16	0.93
RFS3	1475	0.21	0.63	0.89	2.20	0.96
RFS3	1525	0.22	0.66	0.85	2.20	0.94
CSFS1	1500	0.23	0.72	0.96	2.02	0.92
CSFS1	1550	0.24	0.70	0.94	2.11	0.94
CSFS2	1605	0.26	0.69	0.78	2.07	0.87
CSFS2	1650	0.28	0.66	0.81	2.14	0.79
KFS1	1400	0.22	0.78	0.97	1.92	0.98
BFS1	1550	0.27	1.08	1.00	1.93	0.77
BFS2	1300	0.26	1.10	1.00	1.93	0.90
BFS2	1500	0.27	1.09	0.97	1.96	0.83
SFS2	1525	0.29	1.14	1.02	1.96	0.77
LFS1	1400	0.29	1.05	1.14	1.97	0.85
LFS2	1300	0.28	1.08	1.07	2.08	0.92
LFS2	1350	0.28	1.06	1.07	2.03	0.90

Note: I.S. = isomer shift, Q.S. = quadrupole splitting.

routine PC-MOS (copyright CMTE Electronik, Riemerling, FRG) using Lorentzian line shapes. The results are presented in Table 1.

After viscometry the samples were poured from viscometry crucibles onto a stainless-steel plate for cooling. Chips (≃5 g) of the postviscometry samples were analyzed for major-element composition at the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy, France. Analytical methods and errors are included in Table 2.

RESULTS

The viscosity-temperature relationships of the silicate melts are presented in Table 3. Direct comparison of the results for melts with 75, 67, and 50 mol% SiO_2 is made in Figures 1a, 1b, and 1c, respectively. The viscosities of the ferrosilicate melts range over five orders of magnitude in the temperature range investigated. At high temperature (>1400 °C) and from 75 to 67 to 50 mol% SiO_2, the viscosities range over approximately one order of magnitude as the cation is changed from Cs to Li. In the temperature and composition range of this study, viscosity decreases in the order Cs > Rb > K > Na > Ba > Sr > Ca > Mg > Li. Similarly, high-temperature Arrhenian activation energies decrease in the same order.

Table 2. Chemical analyses (wt%)

Sample	(X)O, $(X)_2O$	Fe_2O_3	SiO_2	Total
CSFS1	34.95 (Cs)	20.57	44.54	100.06
CSFS2	39.43 (Cs)	23.84	36.73	100.65
RFS1	25.65 (Rb)	22.76	51.59	97.98
RFS2	30.89 (Rb)	27.53	41.57	98.21
RFS3	38.79 (Rb)	35.03	26.18	97.21
KFS1	16.19 (K)	27.91	55.82	99.52
KFS2	19.79 (K)	34.75	45.39	99.93
KFS3	24.58 (K)	45.07	30.35	100.66
LFS1	5.45 (Li)	29.17	65.43	100.05
LFS2	7.09 (Li)	38.11	54.80	99.72
LFS3	9.67 (Li)	51.59	38.74	100.19
BFS1	22.90 (Ba)	23.91	53.19	98.95
BFS2	27.75 (Ba)	29.20	43.06	99.22
BFS3	35.09 (Ba)	37.22	27.69	98.77
SFS2	20.56 (Sr)	31.93	47.50	99.59
SFS3	25.09 (Sr)	42.82	32.10	99.45
MFS1	11.84 (Mg)	50.10	38.05	100.87

Note: Si by colorimetry; maximum relative error 0.5%. All others by atomic absorption; maximum relative errors are 0.5% (Li, Rb, Cs), 0.9% (Fe), 1.0% (Mg, K), and 2.0% (Ba, Sr).

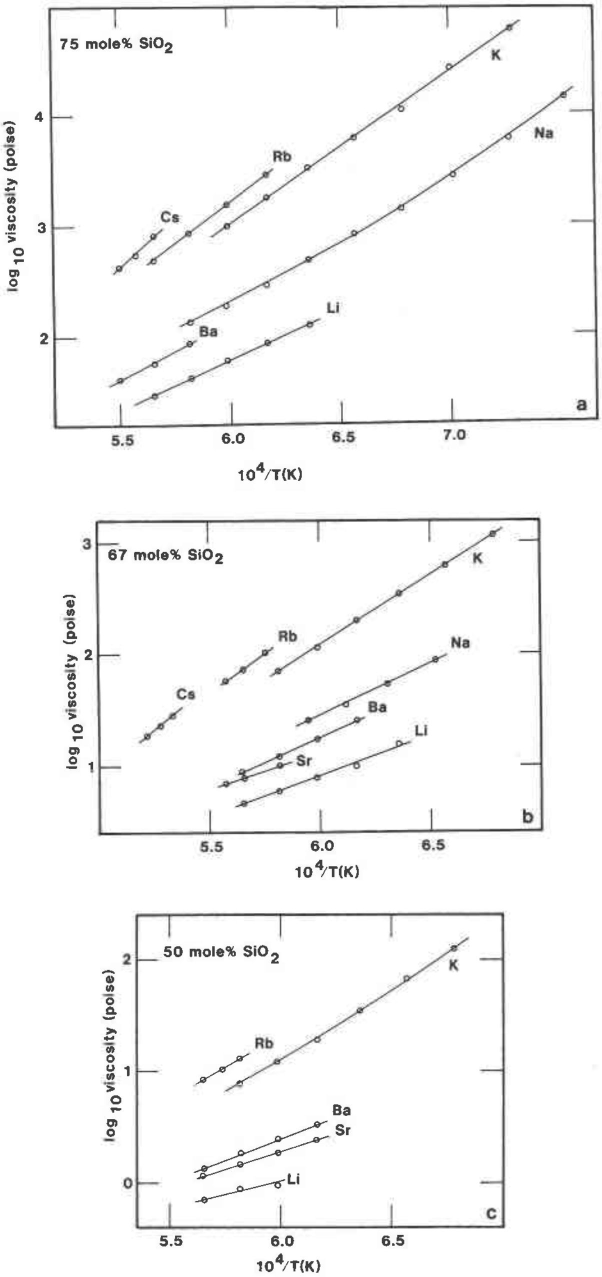

Fig. 1. The viscosity-temperature relationships of alkali and alkaline-earth ferrosilicate melts at (**a**) 75 mol% SiO_2, (**b**) 67 mol% SiO_2, and (**c**) 50 mol% SiO_2.

TABLE 3. Viscosity data ($\log_{10}\eta$ η in poises)

Temp. (°C)	CSFS1	CSFS2	RFS1	RFS2	RFS3	KFS1	KFS2	KFS3	BFS1	BFS2	BFS3
1643	—	1.27	—	—	—	—	—	—	—	—	—
1619	—	1.37	—	—	—	—	—	—	—	—	—
1599	—	1.45	—	—	—	—	—	—	—	—	—
1545	2.63	—	—	—	—	—	—	—	1.62	—	—
1520	2.73	—	—	1.76	—	—	—	—	—	—	—
1496	2.91	—	2.69	1.86	0.914	—	—	—	1.76	0.953	0.123
1471	—	—	—	—	1.02	—	—	—	—	—	—
1446	—	—	2.94	2.01	1.11	—	1.85	0.887	1.94	1.09	0.284
1397	—	—	3.19	2.14	—	3.01	2.06	1.09	—	1.24	0.394
1348	—	—	3.46	—	—	3.25	2.30	1.29	—	1.41	0.521
1299	—	—	—	—	—	3.52	2.54	1.54	—	—	—
1250	—	—	—	—	—	3.79	2.79	1.83	—	—	—
1200	—	—	—	—	—	4.09	3.06	2.10	—	—	—
1151	—	—	—	—	—	4.41	—	—	—	—	—
1102	—	—	—	—	—	4.76	—	—	—	—	—

	SFS2	SFS3	CFS4	CFS5	MFS1	LFS1	LFS2	LFS3
1545	—	—	—	—	—	—	—	—
1520	0.847	—	—	—	−0.0910	—	—	—
1496	0.904	0.0773	—	−0.505	−0.0875	1.47	0.679	−0.156
1446	1.01	0.171	0.184	−0.422	0.0320	1.63	0.784	−0.0220
1397	—	0.269	0.306	−0.346	0.0506	1.78	0.897	0.124
1348	—	0.382	0.433	—	—	1.94	1.01	—
1299	—	—	—	—	—	2.10	1.20	—

Note: Viscosity data are accurate to ±5%.

The viscosity-temperature relationships of the heavy-alkali ferrosilicates (Cs, Rb, and K) cluster relatively tightly in Figures 1a–1c as do the viscosity-temperature relationships of the alkaline-earth ferrosilicates (Ba, Sr, Ca, and Mg). In contrast, the viscosity-temperature relationships of the Na and Li ferrosilicates drop away from the other alkali ferrosilicate data so strongly that the viscosity range of the alkali ferrosilicate melts spans that of the alkaline-earth ferrosilicate melts.

DISCUSSION

Redox considerations

The oxidation-state data of Table 1 indicate that some of the ferrosilicate melts of this study were highly oxidized during viscometry. The Fe^{2+} contents of the glasses obtained by dip quenching range from 2 to 23% of the total Fe contents. The presence of Fe^{2+} in these quenched liquids reduces the mole fraction of oxygen in these liquids, and thus the 8O, 3Si stoichiometry of the base (fully oxidized) compositions is altered. The effect of reducing the oxygen mole fraction on the viscosity of silicate melts has been studied previously by several workers (Williamson et al., 1968; Cukierman and Uhlmann, 1974; Toguri et al., 1976; Klein et al., 1983; Seki and Oeters, 1984; Dingwell and Virgo, 1987, 1988b). The description of viscosity-redox relationships is not yet complete. In compositionally simple melts, the effect of melt reduction (i.e., reduction of oxygen content) on viscosity depends, at least, on the identity of the network-stabilizer cation and the redox ratio, and Dingwell and Virgo (1988b) have proposed a model to relate these effects to melt polymerization, expressed as the ratio of nonbridging oxygens to tetrahedrally coordinated cations (NBO/T). With the use of this model, the viscosities of the alkali ferrosilicates of this study are predicted to be lower than their fully oxidized equivalents. The case is less clear for the alkaline-earth ferrosilicates, but the effect of reduction is predicted to be smaller for these compositions. In general the "redox effects" on viscosity that have been observed to date are 0.3 to 0.6 $\log_{10}$ units and thus are significant compared with the range of viscosities exhibited in Figures 1a–1c (see Dingwell and Virgo, 1987, for a summary). The largest effect expected, and thus the largest correction to be considered in estimating fully oxidized melt viscosities, is for the alkali ferrosilicate melts. These melts, however, are the most highly oxidized in the present study, and so the correction is diminished accordingly. The relative viscosities of the alkali ferrosilicate melts and the alkaline-earth ferrosilicate melts are not expected to change (when compared at fully oxidized conditions) because of these redox effects (Dingwell and Virgo, 1988b). $LiFeSi_3O_x$ melt is the exception, and a possible explanation of this is discussed below.

Structural parameters

It has been known for some time that one effect of substituting alkali or alkaline-earth, network-stabilizing, cations of progressively higher field strength in aluminosilicate liquids of tectosilicate stoichiometry is to reduce the shear viscosity of such liquids (e.g., Bottinga and Weill, 1972). Because all the oxygens in such melt compositions are stoichiometrically constrained to form bridging bonds between tetrahedral cations, the structures are said to be fully polymerized. The structure of such polymerized melts could represent a considerable simplification of the case for partially depolymerized melts

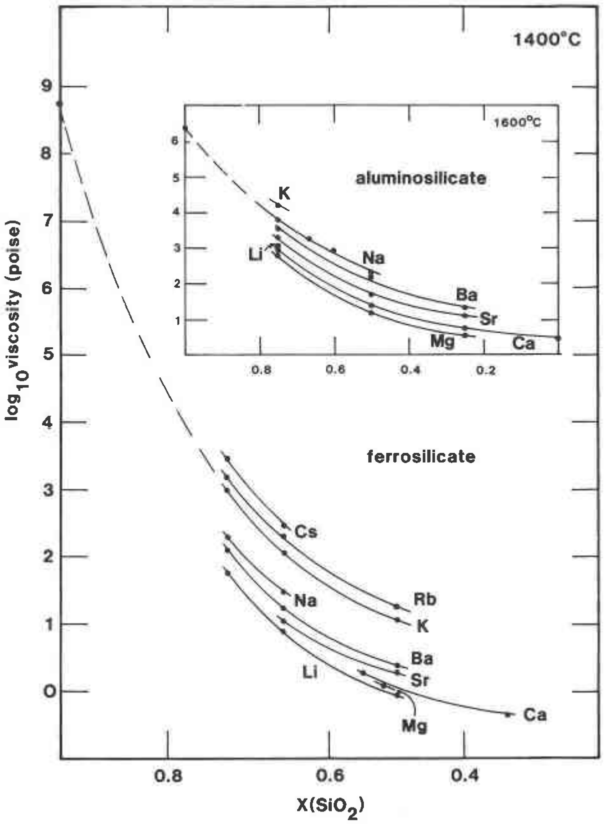

Fig. 2. The effect of the network-stabilizing (alkali or alkaline-earth) cation on the viscosity of ferrosilicate melts. The inset illustrates equivalent data (at 1600 °C) for aluminosilicate melts (aluminosilicate data from Urbain et al., 1982).

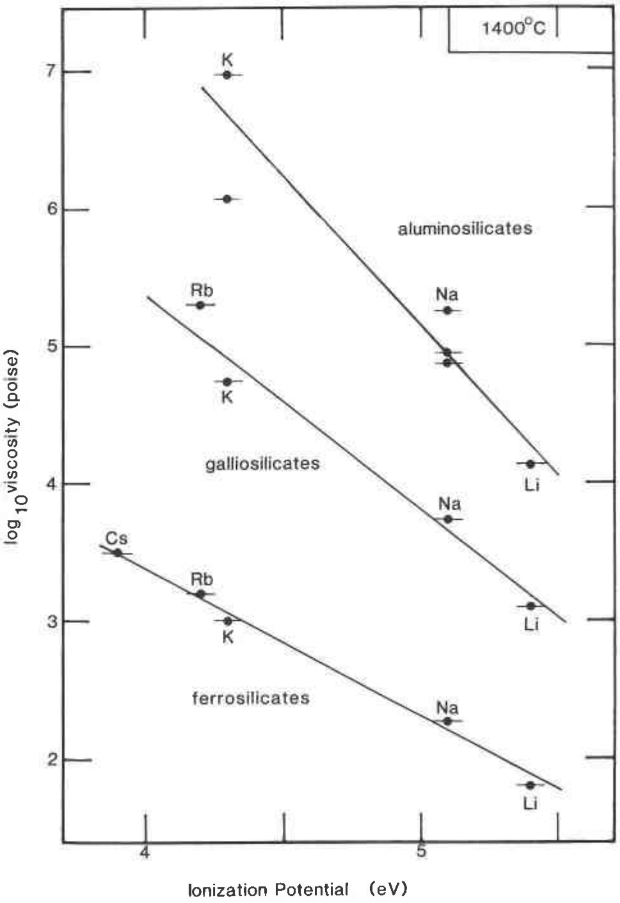

Fig. 3. The viscosity of aluminosilicate, galliosilicate, and ferrosilicate melts as a function of the ionization potential of the network-stabilizing alkali cation. Aluminosilicate viscosity data are from Kozu (1935) (higher) and Urbain et al. (1982) (lower) for orthoclase melt and from Riebling (1966) (lower), Scarfe et al. (1983) (intermediate), and Urbain et al. (1982) (higher) for albite melt; data for the galliosilicates are from Dingwell (in preparation).

because the number and distribution of nonbridging oxygen bonds need not be considered. A number of workers have discussed the possible melt-structure implications of this viscosity-composition trend in terms of the effect of alkali aluminate and alkaline-earth aluminate components on bond strengths and angles in the network structure of silicate and aluminate tetrahedra (Navrotsky et al., 1982, Urbain et al., 1982; Navrotsky et al., 1985; Ryerson, 1985). Recently, Dingwell and Virgo (1987) have pointed out that the exchange of trivalent cations of successively higher electronegativity (Al, Ga, Fe, B) yields a similar trend of decreasing viscosity.

Figure 2 compares the relative viscosities of the ferrosilicate melts of this study (at 1400 °C) with the relative viscosities of the stoichiometrically equivalent aluminosilicate melts [at 1600 °C with data from Urbain et al. (1982) and $LiAlSi_3O_8$ data from Dingwell (unpublished)]. The same trend of relative viscosities exists for both the aluminosilicate and ferrosilicate data. The exception is the behavior of $LiFeSi_3O_x$. The effect of melt reduction on alkali ferrosilicate melt viscosities could explain the observation that the $LiFeSi_3O_x$ melt viscosity is lower relative to the other ferrosilicate melts of Figure 2 than the equivalent $LiAlSi_3O_8$ melt with respect to the other aluminosilicate melts of Figure 2 (inset) because $LiFeSi_3O_x$ is relatively reduced compared with the alkali ferrosilicate melts of equivalent SiO_2 content.

The present study illustrates that the alkali and alkaline-earth substitutions in highly polymerized ferrosilicate melts also produce a trend of decreasing viscosity with increasing field strength, and thus it is reasonable to seek a common origin for the viscosity trends in both the aluminosilicate and ferrosilicate systems.

It has been suggested that the property of the alkali or alkaline-earth cation (network stabilizer) that is of greatest significance in these open-structured liquids is the electron-drawing power of this "stabilizer" cation (Seifert et al., 1982; McMillan et al., 1982; Navrotsky et al., 1985). It is this property that will determine how strongly the stabilizer cation perturbs the T–O–T bridging bond angle between Al and a Si atom. In order to rationalize the composition dependence of viscosity in terms of the true electronegativity of these stabilizer cations in the silicate liquid structure, a measure of cationic electronegativity is required. The field strength, defined as the ratio of ionic radius to charge or radius to charge squared, requires the assumption of a coordination number in selecting the value of the ionic radius. Coordination numbers can be poorly defined for alkalis and alkaline earths in silicate melts. Tabulated values of electronegativity may not necessarily provide a good estimate of the covalent-bonding considerations in silicate glasses. Hess (1980) has proposed the use of ionization potential for this purpose. Figure 3 plots the 1400 °C viscosity of the alkali ferrosilicate liquids versus the ionization potential of the stabilizer cation. The result is a linear correlation of negative slope. Similarly, data for the equivalent alkali aluminosilicate and alkali galliosilicate melts are plotted. The viscosity data for aluminosilicate and galliosilicate melts follow a similar, linear trend of decreasing viscosity with increasing ionization potential of the stabilizer cation. Figure 3 is suggestive that the relative viscosities of alkali aluminosilicate, ferrosilicate, and galliosilicate melts may be attributed to a common structural control.

Thermochemistry

In a series of studies on the thermochemistry of silicate glasses, Navrotsky and coworkers (Navrotsky et al., 1980; Navrotsky et al., 1982; Roy and Navrotsky, 1984) have developed a database for the heat of solution of aluminosilicate glasses in lead borate ($Pb_2B_2O_5$) melt at 973 K using the transposed drop method. Relative differences in heat of solution have been interpreted as relative differences in the strength of bonding in the silicate glasses. Dingwell and Virgo (1988a) illustrated that such heat-of-solution data for alkali and alkaline-earth aluminosilicate compositions (based on a $X^{n+}_{(1/n)}AlSi_3O_8$ stoichiometry, where X = alkali or alkaline-earth cation) yield a smooth relationship versus $\log_{10}$ viscosity of the equivalent liquids at 1400 °C. Similarly, DeYoreo and Navrotsky (1988) have recently obtained heat-of-solution data for $NaFeO_2$-SiO_2 and $NaGaO_2$-SiO_2 glasses and compared these with previous data for $NaAlO_2$-SiO_2 and $NaBO_2$-SiO_2 glasses. DeYoreo and Navrotsky observed a linear dependence of the heat of solution on the inverse of the difference between the field strengths of Si and the trivalent cation. They interpreted this in a manner consistent with the previous discussions by Navrotsky et al. (1985), specifically that an increase in the field strength of the trivalent cation leads to a distortion of T–O–T angles from the SiO_2 optimum angle and consequently to a weakening of the tetrahedral structure of the melt. Comparison with viscosity data available for these compositions (e.g., Urbain et al., 1982; Tait et al., 1984; Dingwell and Virgo, 1988a; Dingwell, in preparation) illustrates that viscosity is lowered with the substitution of cations of increasing electronegativity (Dingwell and Virgo, 1988a), consistent with the interpretation that the tetrahedral structure is weakened. Heat-of-solution data are now required for the equivalent ferrosilicate and galliosilicate glasses to test further the generality of this relationship for glasses and liquids of tectosilicate composition.

The parameterizations of the composition-dependence of tectosilicate melt viscosity provided by this study combined with a recent analysis of the time scale of viscous relaxation in silicate melts (Dingwell and Webb, 1989) support the proposal that viscous flow in the relaxed, liquid state of these melts proceeds by the relatively simple mechanism of oxygen jumps because the frequency of shear-induced jumps (i.e., viscous flow) is much less than the frequency of thermal motion (self-diffusivity) in the relaxed region. The compositional dependence of viscosity can be visualized as the effect of cation–oxygen bond strength on the mobility of oxygen atoms.

CONCLUSION

Aluminosilicate, ferrosilicate, and galliosilicate melts represent a structurally simplified subset of silicate melts whose relative viscosities may be understood in terms of the relative mean bond strengths in these liquids. The viscosities of these melts, compared at equal SiO_2 contents, decrease with increasing electronegativity (measured with ionization energy) of the network-stabilizer and the network-former cations. The observation that the Newtonian viscosity is controlled by the mean strengths of cation–oxygen bonds is consistent with the hypothesis that the viscous-flow process in the relaxed liquid state is rate-limited by the effect of these bond strengths on the mobility of oxygen atoms (Dingwell and Webb, 1989).

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