

## Shear viscosities of galliosilicate liquids

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### ABSTRACT

The shear viscosities of 19 galliosilicate and related liquids have been measured using the concentric cylinder method. Nine of the liquid compositions lie in the  $\text{Na}_2\text{O}-\text{Ga}_2\text{O}_3-\text{SiO}_2$  system, eight liquids correspond in composition to  $X_{1/n}^+\text{GaSi}_3\text{O}_8$  (where  $X = \text{Cs, Rb, K, Na, Li, Ba, Sr, and Ca}$ ), and five liquids are Li silicates related by the exchange of Al, Ga, and Fe. The measurements were performed at 1 atm of air pressure in the temperature range of 1700–900 °C and a viscosity range of  $10^{1.3}$ – $10^5$  dPaS. The rotation rates ranged from 0.5 to 100 rpm.

All melts exhibited Newtonian viscosities. The viscosities of the  $X_{1/n}^+\text{GaSi}_3\text{O}_8$  liquids decrease in the order  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$  and  $\text{Ba} > \text{Sr} > \text{Ca}$ . Increasing  $\text{SiO}_2$  content in liquids on the  $\text{SiO}_2$ - $\text{NaGaO}_2$  join ( $\text{NaGaSiO}_4$ ,  $\text{NaGaSi}_2\text{O}_6$ ,  $\text{NaGaSi}_3\text{O}_8$ ) results in increasing viscosity. The exchange of  $\text{Ga}_2\text{O}_3$  for  $\text{Na}_2\text{O}$  along the 75 mol%  $\text{SiO}_2$  isopleth ( $\text{Na}_2\text{Si}_3\text{O}_7$ ,  $\text{Na}_{1.5}\text{Ga}_{0.5}\text{Si}_3\text{O}_{7.5}$ ,  $\text{NaGaSi}_3\text{O}_8$ ,  $\text{Na}_{0.5}\text{Ga}_{1.5}\text{Si}_3\text{O}_{8.5}$ ,  $\text{Ga}_2\text{Si}_3\text{O}_9$ ) yields a viscosity maximum at  $\text{NaGaSi}_3\text{O}_8$ . Comparison with viscosity data for aluminosilicate, ferrosilicate, and borosilicate liquids indicates that viscosities decrease in the order aluminosilicate > galliosilicate > ferrosilicate > borosilicate. Recent heat of solution measurements on  $\text{NaXSi}_3\text{O}_8$  glasses (where  $X = \text{Al, Fe, Ga, and B}$ ), in molten  $\text{Pb}_2\text{B}_2\text{O}_5$  at 973 K indicate that the degree to which glasses are stabilized increases in the order  $\text{Al} > \text{Ga} > \text{Fe} > \text{B}$  (DeYoreo et al., 1990). Thus a correlation can be made between liquid viscosity and glassy heat of solution that is similar to that previously noted for the alkali exchange in aluminosilicate melts of the formula  $\text{XAlSi}_3\text{O}_8$  (where  $X = \text{alkali}$ ). Galliosilicate liquids have been used as structural analogues of the aluminosilicates. The composition-dependence of their viscosities is analogous to the aluminosilicates with the difference that the glass transition occurs at much lower temperatures in galliosilicate liquids. These results confirm galliosilicate liquids as useful analogues for aluminosilicate liquids in studies where the high viscosities of the latter may prevent experimental determination of certain relaxed liquid properties.

### INTRODUCTION

Viscosity is possibly the most diagnostic property of a liquid. It has been demonstrated recently that the time scale of relaxation associated with viscous flow closely matches the mean lifetime of individual Si-O bonds in silicate liquids (Liu et al., 1988). Farnan and Stebbins (1990) have recently calculated viscosity from  $^{29}\text{Si}$  NMR relaxation time data. The relaxation behavior of silicate liquids can be approximated from the ratio of viscosity to elastic modulus, i.e., the Maxwell relation (e.g., Angell and Torrell, 1983). The relative composition and temperature invariance of the elastic modulus yields the approximation that viscosity is a linear measure of the time scale of bond exchange that dominates high-temperature melt kinetics and defines the glass transition (Dingwell and Webb, 1989).

Fundamentally then, viscosity is a measure of melt dynamics, but the dynamics themselves must correlate with the strength of bonds and distribution of cations in silicate melts. One source of information on the static structure of silicate melts is the relative enthalpies of silicate

glasses. Relative enthalpies of silicate glasses are available for a wide range of compositions from the systematic studies of Navrotsky and coworkers using lead borate solution studies (e.g., Roy and Navrotsky, 1984). A recent comparison of relative heats of solution of Na aluminosilicate, gallio-, ferro-, and borosilicate glasses (DeYoreo et al., 1990) provides data that enable comparison with the present shear viscosity data.

Gallium has been used as a structural analogue for Al in several studies of the properties and structure of silicate liquid and glass (e.g., Fleet et al., 1984; Henderson et al., 1985; Matson and Sharma, 1985; Dickenson and Hess, 1986; Sherriff and Fleet, 1990). The present study illustrates some of the similarities in properties of galliosilicates and aluminosilicates. However, one important difference is the lower viscosities of the galliosilicates that reduce the temperatures required for several types of experimental investigations of melt properties.

### EXPERIMENTAL METHOD

Eight of the compositions used in this study are based on a stoichiometry given by the general formula

TABLE 1. Glass analyses (wt%)

Sample	XO, X <sub>2</sub> O	Ga <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Total
NGS1	9.22(Na)	30.72	61.04	100.98
NGS2	4.40	38.10	57.88	100.38
NGS3	—	36.44	63.76	100.20
NGS4	16.08	13.34	70.07	99.49
NGS5	12.49	39.01	50.26	101.76
NGS6	22.69	—	74.58	97.27
NGS7	10.82	35.59	55.08	101.49
NGS8	18.20	50.82	31.82	100.84
CSGS1	34.31(Cs)	22.51	44.53	101.35
RGS1	24.05(Rb)	25.47	48.40	97.92
KGS1	14.27(K)	28.26	56.68	99.21
LGS1	3.88(Li)*	32.93	63.19	100.00
BGS1	23.02(Ba)	26.33	51.10	100.45
SGS1	17.06(Sr)	31.55	51.71	100.32
CGS1	8.56(Ca)	30.79	60.28	99.63

	Li <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	FeO	Al <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Total
LAGS1	5.58	—	—	10.18	18.50	67.51	101.77
LFGS1	5.30	10.19	3.48	—	16.98	64.39	100.34
LAFS1	5.74	10.83	4.63	10.19	—	67.73	99.12

\* Li<sub>2</sub>O (theoretical), see text for operating conditions. Averages of 10 analyses. Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio obtained using <sup>57</sup>Fe Mössbauer spectroscopy.

$X_{1+n}^{n+}GaSi_3O_8$  (where X is Cs, Rb, K, Na, Li, Ba, Sr, Ca). Seven of the compositions lie in the Na<sub>2</sub>O-Ga<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. Five of these are on the Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>-Ga<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> join (Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>, Na<sub>1.5</sub>Ga<sub>0.5</sub>Si<sub>3</sub>O<sub>7.5</sub>, NaGaSi<sub>3</sub>O<sub>8</sub>, Na<sub>0.5</sub>Ga<sub>1.5</sub>Si<sub>3</sub>O<sub>8.5</sub>, Ga<sub>2</sub>Si<sub>3</sub>O<sub>9</sub>) and three are on the SiO<sub>2</sub>-NaGaO<sub>2</sub> join (NaGaSi<sub>3</sub>O<sub>8</sub>, NaGaSi<sub>2</sub>O<sub>6</sub>, NaGaSiO<sub>4</sub>). Six of the compositions are Li silicates involving the exchange of Fe, Ga, and Al [Li(Ga,Fe,Al)Si<sub>3</sub>O<sub>8</sub>]. These compositions were chosen to permit comparison with existing shear viscosity data for aluminosilicate and ferrosilicate melts of equivalent stoichiometry (Riebling, 1966; Hunnold and Brückner, 1980; Urbain et al., 1982; Dingwell, 1989b), with low temperature data of Lapp and Shelby (1986a, 1986b) and Piguet and Shelby (1985), and with the heat-of-solution data of DeYoreo et al. (1990). The starting materials for the preparation of glasses were Cs<sub>2</sub>CO<sub>3</sub> (99.9%), Rb<sub>2</sub>CO<sub>3</sub> (99%), K<sub>2</sub>CO<sub>3</sub> (99%), Na<sub>2</sub>CO<sub>3</sub> (99%), Li<sub>2</sub>CO<sub>3</sub> (99%), Ga<sub>2</sub>O<sub>3</sub> (99.99%), BaCO<sub>3</sub> (99%), SrCO<sub>3</sub> (99%), CaCO<sub>3</sub> (99%), Fe<sub>2</sub>O<sub>3</sub> (99%), Al<sub>2</sub>O<sub>3</sub> (99%), and SiO<sub>2</sub> (99.9%). The carbonate and oxide powders were kept in an oven at 200 °C prior to use. Powder mixtures equivalent to 100 g of dehydrated and decarbonated melt were weighed into 500-ml plastic bottles and mixed by agitation for approximately 5 min. The mixed powders were loaded stepwise into a 75-ml Pt<sub>95</sub>Au<sub>5</sub> crucible and melted directly at temperatures from 1200 to 1700 °C. Some of the batches were removed rapidly from the batch furnace and poured directly from the 75-ml crucibles into the viscometry crucibles. The remainder of the batches were removed from the batch furnace and allowed to cool in the 75-ml crucibles. These batches were subsequently broken from these crucibles with a hammer, and the chips were remelted stepwise into the viscometry crucibles.

The shear viscosities were measured at 1 atm and at temperatures in the range of 1700–900 °C in air, using

the concentric cylinder method. The apparatus is that described in previous work (Dingwell, 1989a, 1989b). The viscometry furnace is a box furnace with MoSi<sub>2</sub> heating elements. The viscometry crucibles and spindle, fabricated from Pt<sub>80</sub>Rh<sub>20</sub>, are identical to those described by Dingwell and Virgo (1988). The viscometer heads are Brookfield models HBT and RVT (with full-scale torques of  $5.75 \times 10^{-1}$  and  $7.20 \times 10^{-2}$  Nm, respectively). The measurements of viscosity are relative. The values of torque are converted to viscosity values based on a family of viscosity-torque calibration curves obtained from viscosity measurements of Deutsche Glastechnische Gesellschaft standard DGG1. The precision of these measurements is  $\pm 2.5\%$  at  $2\sigma$ . The calibration using viscosity standards yields an accuracy of  $\pm 5\%$  at  $2\sigma$ .

The rotation rates vary with 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 Newtonian viscosities resulting from this observation are consistent with the proposal that the time scale of structural relaxation for melts of these viscosities is much shorter than the inverse of the experimental strain rate. Thus we are measuring what may be usefully defined as liquid rather than glassy properties.

Measurements were made starting with the highest temperatures and reducing the control temperature in steps of 50, 25, or 20 °C until an instrumental or sample limit was reached. The last measurement was always a reoccupation of the highest temperature determination. No difference was observed between first and last viscosity determinations, indicating that no compositional or instrumental drift took place during the viscometry determinations.

The oxidation state of the Fe-bearing liquids was determined on small dip-quenched samples with <sup>57</sup>Fe Mössbauer spectroscopy using the method described in Dingwell (1989b).

After viscometry, the samples were cooled in the viscometry furnace, removed, and remelted in the batch furnace. They were allowed to pour into a 75-cm<sup>3</sup> Pt<sub>95</sub>Au<sub>5</sub> crucible in the batch furnace or poured onto a stainless steel plate upon removal from the batch furnace. The experimental products were analyzed with a Cameca SX 50 electron microprobe using wavelength dispersive analysis. The operating conditions were accelerating voltage of 15 kV, a sample current of 15 nA on brass, a defocused beam diameter of 30 μm and count times of 20 s. The standards were diopside (Ca), orthoclase (K), albite (Na,Si), synthetic MgGa<sub>2</sub>O<sub>4</sub> spinel (Ga), Fe<sub>2</sub>O<sub>3</sub> (Fe), albite (Al) and synthetic glasses CSFS1 (Cs), RFS1 (Rb), BFS2 (Ba), SFS2 (Sr) (Dingwell, 1989b). The results are in Table 1.

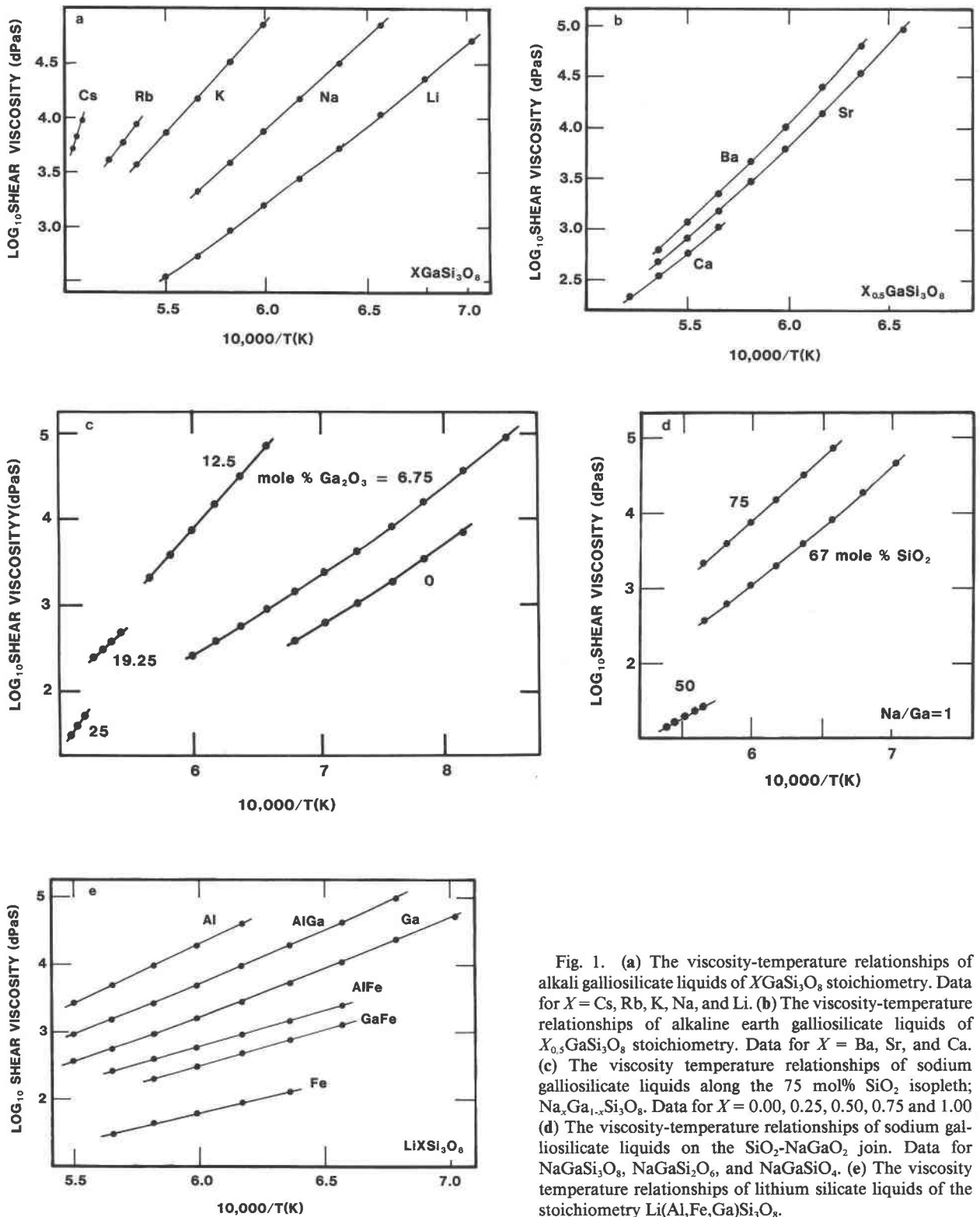


Fig. 1. (a) The viscosity-temperature relationships of alkali galliosilicate liquids of  $X\text{GaSi}_3\text{O}_8$  stoichiometry. Data for  $X = \text{Cs}, \text{Rb}, \text{K}, \text{Na},$  and  $\text{Li}$ . (b) The viscosity-temperature relationships of alkaline earth galliosilicate liquids of  $X_{0.5}\text{GaSi}_3\text{O}_8$  stoichiometry. Data for  $X = \text{Ba}, \text{Sr},$  and  $\text{Ca}$ . (c) The viscosity-temperature relationships of sodium galliosilicate liquids along the 75 mol%  $\text{SiO}_2$  isopleth;  $\text{Na}_x\text{Ga}_{1-x}\text{Si}_3\text{O}_8$ . Data for  $X = 0.00, 0.25, 0.50, 0.75$  and 1.00. (d) The viscosity-temperature relationships of sodium galliosilicate liquids on the  $\text{SiO}_2$ - $\text{NaGaO}_2$  join. Data for  $\text{NaGaSi}_3\text{O}_8, \text{NaGaSi}_2\text{O}_6,$  and  $\text{NaGaSiO}_4$ . (e) The viscosity-temperature relationships of lithium silicate liquids of the stoichiometry  $\text{Li}(\text{Al}, \text{Fe}, \text{Ga})\text{Si}_3\text{O}_8$ .

TABLE 2. Viscosity data ( $\log_{10}\eta$ , in dPaS)

T (°C)	CSGS1	RGS1	KGS1	NGS1	LGS1	BGS1	SGS1	CGS1	NGS2	NGS3
1712	3.72	—	—	—	—	—	—	—	—	—
1702	3.83	—	—	—	—	—	—	—	—	—
1692	3.98	—	—	—	—	—	—	—	—	2.53
1672	—	—	—	—	—	—	—	—	—	2.64
1653	—	—	—	—	—	—	—	—	—	2.78
1643	—	3.62	—	—	—	—	—	2.33	2.40	—
1618	—	3.78	—	—	—	—	—	—	2.49	—
1594	—	3.95	3.57	—	—	2.80	2.68	2.54	2.58	—
1569	—	—	—	—	—	—	—	—	2.70	—
1545	—	—	3.87	—	2.55	3.07	2.91	2.76	2.87	—
1520	—	—	—	—	—	—	—	—	—	—
1495	—	—	4.18	3.33	2.74	3.35	3.18	3.02	—	—
1446	—	—	4.52	3.59	2.97	3.67	3.47	—	—	—
1397	—	—	4.86	3.88	3.20	4.01	3.79	—	—	—
1348	—	—	—	4.18	3.45	4.40	4.14	—	—	—
1298	—	—	—	4.51	3.73	4.81	4.54	—	—	—
1249	—	—	—	4.86	4.04	—	4.96	—	—	—
1200	—	—	—	—	4.37	—	—	—	—	—
1151	—	—	—	—	4.72	—	—	—	—	—

T (°C)	NGS4	NGS5	NGS6	NGS7	NGS8	NGS9	LAGS1	LFGS1	LAFS1
1712	—	—	—	—	—	1.50	—	—	—
1692	—	—	—	—	—	1.60	—	—	—
1672	—	—	—	—	—	1.72	—	—	—
1653	—	—	—	1.34	—	—	—	—	—
1574	—	—	—	—	1.17	—	—	—	—
1554	—	—	—	—	1.23	—	—	—	—
1545	—	—	—	1.43	1.30	—	2.96	—	—
1535	—	—	—	—	1.36	—	—	—	—
1515	—	—	—	—	1.43	—	—	—	—
1496	—	—	—	1.52	—	—	3.18	—	2.42
1471	—	2.57	—	1.61	—	—	—	—	—
1446	—	2.79	—	—	—	—	3.43	2.30	2.60
1397	2.42	3.04	—	—	—	—	3.69	2.48	2.77
1348	2.59	3.30	—	—	—	—	3.98	2.68	2.97
1298	2.77	3.59	—	—	—	—	4.29	2.88	3.17
1249	2.97	3.91	—	—	—	—	4.63	3.11	3.41
1200	3.17	4.27	2.59	—	—	—	4.99	—	—
1151	3.40	4.66	2.80	—	—	—	—	—	—
1102	3.64	—	3.03	—	—	—	—	—	—
1052	3.92	—	3.28	—	—	—	—	—	—
1003	4.22	—	3.55	—	—	—	—	—	—
954	4.58	—	3.86	—	—	—	—	—	—
905	4.97	—	—	—	—	—	—	—	—

Note: Viscosity data are accurate to  $\pm 5\%$  ( $2\sigma$ ).

## RESULTS AND DISCUSSION

The results of the viscometry determinations are presented in Table 2 and Figures 1a–1e. The viscosities of the galliosilicate melts are Arrhenian, within error, over the present experimental temperature range. Thus the temperature dependence of the liquid viscosities can be described using

$$\log_{10}\eta = a + b/T \quad (1)$$

where  $a$  and  $b$  are constants. Table 3 contains the values of  $a$  and  $b$  obtained for the present liquids. The viscosities range in value from  $10^{1.3}$  to  $10^5$  poises. The viscosities and activation energies of these high temperature data decrease through the alkali galliosilicates in the order Cs > Rb > K > Na > Li. The viscosities of the alkaline earth galliosilicates decrease in the order Ba > Sr > Ca with constant activation energy.

The composition dependence of the viscosities of the

galliosilicate melts exhibit similarities to aluminosilicate melts of equivalent stoichiometry (e.g., Urbain et al., 1982). The relative viscosities of the alkali galliosilicates (Cs > Rb > K > Na > Li) and alkaline earth galliosilicates (Ba > Sr > Ca) match those observed for the aluminosilicates and ferrosilicates (Dingwell, 1989b). One possible difference is the relative viscosity of the Na-GaSi<sub>3</sub>O<sub>8</sub> liquid vs. the Ba<sub>0.5</sub>GaSiO<sub>8</sub> melt. The viscosities of the ferrosilicate melts decrease in the order Na > Ba (Fig. 1a of Dingwell, 1989b) but the ferrosilicate data are not extensive enough in temperature to preclude a cross-over, as is observed in this study. Additionally, the ferrosilicate comparison is complicated by the differing oxidation states of the Na and Ba ferrosilicate liquids (Dingwell, 1989b). Equivalent aluminosilicate data (Urbain et al., 1982) illustrate the trend Na > Ba but data are only available at higher temperatures, where this trend would also be observed in the galliosilicate liquids (Fig. 1a). In general it appears that the relative viscosities of

TABLE 3. Arrhenius parameters

Sample	a	b	Number of data
CSGS1	-21.84(0.02)	5.07(0.44)	3
RGS1	-8.95(0.01)	2.41(0.05)	3
KGS1	-7.37(0.05)	2.04(0.01)	5
	-6.39(0.04)	1.87(0.01)	6*
NGS1	-6.150(0.005)	1.675(0.006)	6
	-7.07(0.05)	1.827(0.01)	7*
LGS1	-5.35(0.02)	1.43(0.02)	9
BGS1	-7.91(0.02)	1.99(0.03)	7
SGS1	-7.46(0.03)	1.88(0.03)	8
CGS1	-5.893(0.008)	1.56(0.03)	4
NGS2	-5.025(0.009)	1.42(0.06)	4
NGS3	-9.81(0.01)	2.42(0.19)	3
NGS4	-3.66(0.04)	1.01(0.01)	11
NGS5	-6.10(0.03)	1.53(0.02)	8
NGS6	-3.731(0.009)	0.930(0.008)	6
NGS7	-5.0100(0.0007)	1.155(0.004)	4
NGS8	-4.661(0.004)	1.07(0.018)	5
NGS9	-9.200(0.007)	2.12(0.099)	3
LAGS1	-5.76(0.01)	1.58(0.01)	8
LFGS1	-3.942(0.005)	1.073(0.009)	5
LAFS1	-3.649(0.008)	1.07(0.01)	6

\* Including low temperature data of Lapp and Shelby (1986a). Numbers in parentheses are 1 standard error.

the alkali vs. the alkaline earth gallio-, ferro-, and aluminosilicates might be temperature-dependent, whereas there is no indication of this within the alkali or alkaline earth groups.

Figure 2 compares the viscosities of the alkali galliosilicate liquids (this study) containing 75 mol% SiO<sub>2</sub> at 1600 °C. Five liquids spanning the compositional range of sodium trisilicate to gallium trisilicate (Na<sub>2</sub>O · 3SiO<sub>2</sub> · Ga<sub>2</sub>O<sub>3</sub> · 3SiO<sub>2</sub>) illustrate a maximum at or near the NaGaSi<sub>3</sub>O<sub>8</sub> composition. This variation of viscosity at constant temperature is similar to that observed by Lapp and Shelby (1986a, 1986b) at much lower temperatures and higher viscosities. It is also similar to the variation of viscosity with composition in the equivalent aluminosilicate liquids, at high temperatures (Riebling, 1966) and low temperatures (Hunnold and Brückner, 1980). The relative viscosities of the alkali galliosilicates of XGaSi<sub>3</sub>O<sub>8</sub> are also illustrated in Figure 2. These data for X = Cs, Rb,

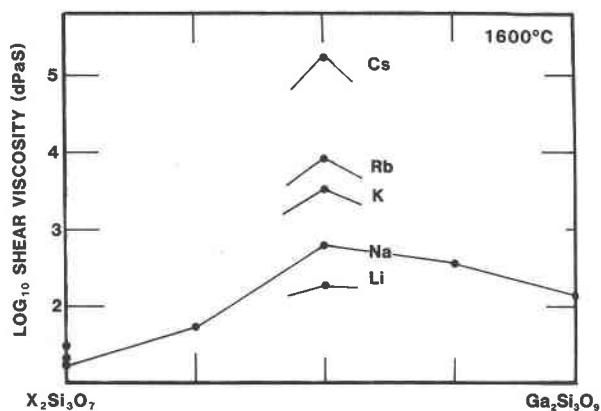


Fig. 2. Viscosities of galliosilicate liquids containing 75 mol% SiO<sub>2</sub> at 1600 °C.

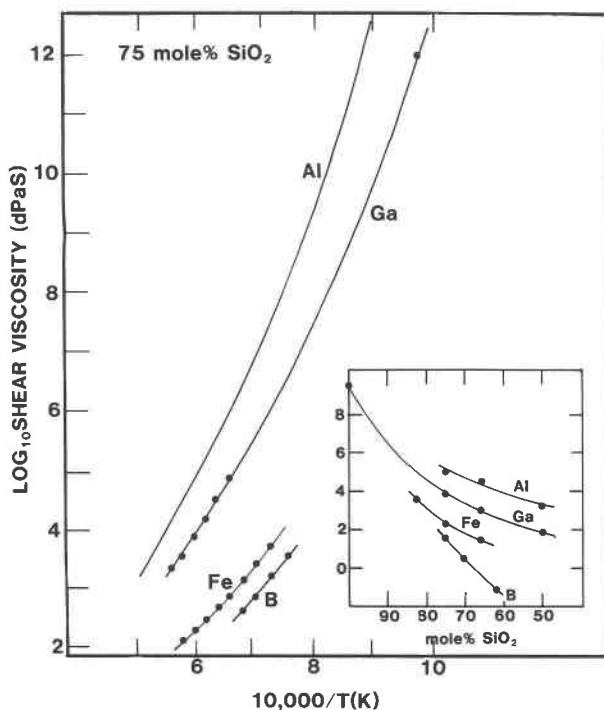


Fig. 3. Comparison of viscosity-temperature relationships for liquids on the join SiO<sub>2</sub>-NaXO<sub>2</sub> (where X = Al, Ga, Fe, and B). Data from this study, galliosilicates; Riebling (1966), aluminosilicates; Tait et al. (1984), borosilicates; and Dingwell and Virgo (1988), ferrosilicates.

K, Na, and Li can be combined with the alkali trisilicate data (left side of Figure 2) and the Ga<sub>2</sub>O<sub>3</sub> · 3SiO<sub>2</sub> data to illustrate how cation specific the relative viscosities on the trisilicate join are. The magnitude of the maximum in viscosity at or near the XGaSi<sub>3</sub>O<sub>8</sub> composition depends strongly on the identity of X. A similar conclusion can be drawn from the low temperature data of Lapp and Shelby (1986b) for potassium and sodium galliosilicates on the trisilicate join.

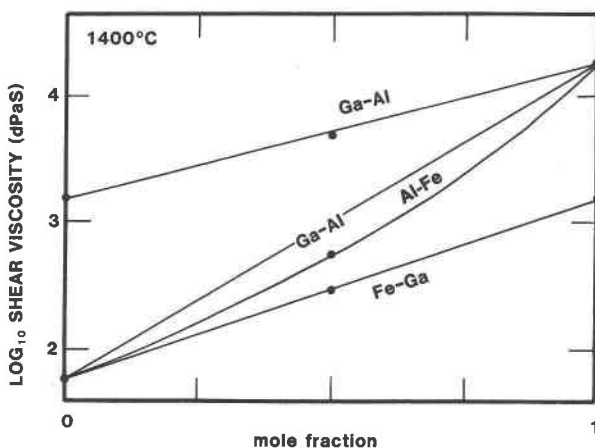


Fig. 4. Isothermal comparison of viscosities of lithium silicate liquids at 1400 °C.

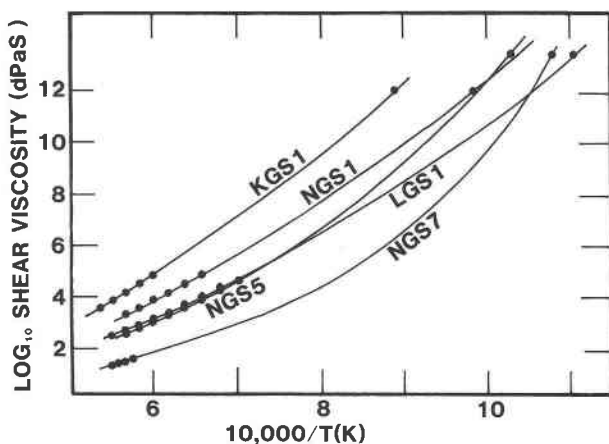


Fig. 5. Low- and high-temperature viscosity data for selected galliosilicates illustrating the non-Arrhenian temperature dependence.

Figure 3 is a comparison of viscosities of liquids along the join  $\text{SiO}_2\text{-NaTO}_2$  (where  $T = \text{Al, Ga, Fe, B}$ ). As discussed by Dingwell and Virgo (1988), the relative viscosities of these liquids may be explained in terms of the increasingly destabilizing effects of Al, Ga, Fe, and B on the strength of O-bridging bonds in the tetrahedral network structure of the liquids. The departure of the borosilicates from the trend exhibited by the gallio-, ferro-, and aluminosilicates may be related to an increasing proportion of B in trigonal coordination in liquids on the  $\text{SiO}_2\text{-NaBO}_2$  join with decreasing  $\text{SiO}_2$  content.

DeYoreo et al. (1990) have measured the heats of solution (in  $2\text{PbO}\cdot\text{B}_2\text{O}_3$ , at 973 K) of glasses on the joins  $\text{NaXO}_2\text{-SiO}_2$  (where  $X = \text{Ga}$  and  $\text{Fe}$ ). These results, compared with data for the equivalent aluminosilicates and borosilicates (Roy and Navrotsky, 1984), illustrate a trend of decreasing enthalpy of solution in the order  $\text{Al} > \text{Ga} > \text{Fe} > \text{B}$ . The relative viscosities of the  $\text{NaXSi}_3\text{O}_8$  melts (this study; Urbain et al., 1982; Dingwell, 1989b) decrease in the same order. This positive correlation between relative enthalpy and viscosity is also observed for the substitution of alkali and alkaline earth cations in melts of the  $\text{SiO}_2\text{-X}^{n+}\text{Y}_n\text{O}_{2n}$  joins (Dingwell and Virgo, 1988), and it is speculated here that heat-of-solution data for the alkali-substituted galliosilicate and borosilicate melts of the present study will also show this enthalpy-viscosity trend.

Figure 1e presents the viscosity data for Li silicate melts involving the exchange of Al, Ga, and Fe for each other. The two Ga-bearing joins,  $\text{LiGaSi}_3\text{O}_8\text{-LiAlSi}_3\text{O}_8$  and  $\text{LiGaSi}_3\text{O}_8\text{-LiFeSi}_3\text{O}_8$  exhibit linear composition dependence of viscosities (Fig. 4). In contrast, the  $\text{LiAlSi}_3\text{O}_8\text{-LiFeSi}_3\text{O}_8$  join has a negative deviation from additivity.

Low-temperature viscosity and glass transition-temperature data for a number of the compositions of this study are available in the literature. The low-temperature viscosity data are combined with the high temperature data of this study in Figure 5. The  $T_g$  data of Lapp and

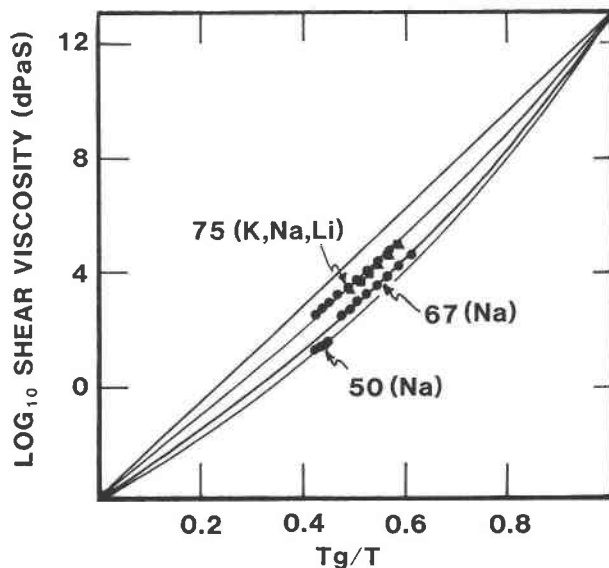


Fig. 6. A strong and fragile liquid plot ( $\log \eta$  normalized to  $T_g/T$ ) for some galliosilicate liquids ( $\eta$  is shear viscosity,  $T_g$  is the  $\log \eta = 13$  isokom).

Shelby (1986a, 1986b) may be converted into viscosity data using relationships among relaxation time, cooling and heating rates, and viscosity (Dingwell and Webb, 1990). The resultant viscosity data are plotted in Figure 5. All the compositions exhibit non-Arrhenian behavior. The data of Figure 5 can be reduced to a simpler comparison using a plot of  $\log_{10}$  shear viscosity vs.  $T_g/T$  (Angell, 1984). This yields a spectrum of curves of strong vs. fragile liquid behavior (Angell, 1984). Figure 6 is such a plot. It can be seen that the  $T_g/T$  normalization reduces the temperature dependence of shear viscosity of the  $\text{KGaSi}_3\text{O}_8$ ,  $\text{NaGaSi}_3\text{O}_8$ , and  $\text{LiGaSi}_3\text{O}_8$  to a single curve. Thus the degree of fragility of these liquids appears to be independent of the identity of the alkali cation. This can be taken to imply that the temperature-induced changes in the structural rearrangements characterizing viscous flow (recorded by the configurational entropy, according to Adam and Gibbs, 1965) in these liquids are only weakly dependent on the identity of the alkali cation. In contrast, decreasing  $\text{SiO}_2$  content from 75 to 50 mol% in the  $\text{SiO}_2\text{-NaGaO}_2$  system increases the fragility of the liquids. The Ga/Si ratio exerts a control on the degree of non-Arrhenian behavior. Similar observations have been made for aluminosilicate liquids (Scamehorn and Angell, 1989).

## SUMMARY

The viscosity-temperature relationships of galliosilicate liquids have been measured at high temperatures using the concentric cylinder method. The composition dependence of viscosities of the galliosilicate liquids are similar to those of equivalent aluminosilicates. Viscosities exhibit intermediate maxima along silica isopleths at or near the composition  $\text{Ga/Na} = 1$ . An increase in the field strength of the alkali or alkaline earth cation decreases

es viscosity. Comparison with previously published low-temperature viscosity data reveals that all the galliosilicate viscosity data are non-Arrhenian functions of temperature. Normalization of the viscosity temperature relationships to  $Tg/T$  simplifies the composition dependence of the viscosity data. The fragility or degree of non-Arrhenian behavior of the galliosilicates is independent of the identity of the alkali cation but dependent on the Ga/Si ratio. A correlation between the heat of solution and shear viscosity noted previously for alkali and alkaline earth exchanges may be qualitatively extended to a comparison of gallium, iron, aluminum, and boron silicates. The galliosilicates should prove useful as analogue compositions for aluminosilicate liquids whose higher viscosities may prevent certain experimental investigations of liquid properties.

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