

Shear viscosity of alkali and alkaline earth titanium silicate liquids

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ABSTRACT

The shear viscosities of 13 silicate liquids along the $\text{Na}_2\text{SiO}_3\text{-TiO}_2$ and $\text{CaSiO}_3\text{-TiO}_2$ joins as well as six liquids based on the sphene stoichiometry $X_{2/n}^{n+}\text{TiSiO}_5$ (where X represents Li, Na, K, Rb, Cs, Ca, and Sr) have been measured in equilibrium with air using the concentric cylinder method. The $\text{Na}_2\text{SiO}_3\text{-TiO}_2$ join was investigated from 10 to 50 mol% TiO_2 in the temperature range 1000–1150 °C, whereas the $\text{CaSiO}_3\text{-TiO}_2$ join was investigated from 10 to 80 mol% TiO_2 in the temperature range of 1400–1625 °C.

The shear viscosities of liquids in the $\text{CaSiO}_3\text{-TiO}_2$ and $\text{Na}_2\text{SiO}_3\text{-TiO}_2$ systems decrease with the addition of TiO_2 . The decrease is linear in the $\text{CaSiO}_3\text{-TiO}_2$ system at 1400–1600 °C but nonlinear in the $\text{Na}_2\text{SiO}_3\text{-TiO}_2$ system at 1000–1150 °C. Viscosities of melts of sphene stoichiometry, $X_{1/n}^{n+}\text{TiSiO}_5$ (where $X = \text{Cs, Rb, K, Na, Li, Ba, Sr, and Ca}$), decrease with increasing field strength. Similar to the behavior of ferro-, alumin-, and galliosilicate melts, this decrease is strong for the alkalis but very weak for the alkaline earths.

INTRODUCTION

TiO_2 is present in major element amounts in most igneous rocks. Although 2–3 wt% TiO_2 is the average value for Cenozoic alkali basalts and basanites (Chayes, 1975), much higher concentrations are found in volcanic rocks of the potassic-ultrapotassic series (Gunter et al., 1990). Foley and Wheller (1990) report values up to 9 wt% TiO_2 from some lamproites, and Mitchell (1991) has analyzed glass inclusions in volcanic sanidine from these rocks containing up to 11 wt% TiO_2 . Although such examples are not very widespread, the unusual geochemistry of these lamproites and continuing discussions of their petrogenesis make the investigation of the TiO_2 component in silicate melts timely for geochemists.

The glass literature is often an abundant source of information on the frozen remains of high-temperature silicate liquids. Analysis of the quench-rate dependence of glass properties opens a window into the temperature dependence of liquid properties (Dingwell and Webb, 1989, 1990). Crystal-free, Ti-bearing glasses are, however, difficult to obtain, and this difficulty may have contributed to some of the controversy surrounding the structural role of TiO_2 in silicate glasses and, by extrapolation, liquids (see Mysen, 1988, for a review).

Thus, in an attempt to evaluate directly the effects of TiO_2 on the physical properties of silicate liquids, the density (Dingwell, 1991, and in preparation) and viscosity (this study) of a series of alkali and alkaline earth silicate liquids have been investigated.

In a more general sense, the investigation of physical properties of TiO_2 -bearing melts provides an indication of the type of effects that variable coordination number for any component may have on the behavior of silicate

melts. The systems $\text{Na}_2\text{SiO}_3\text{-TiO}_2$ and $\text{CaSiO}_3\text{-TiO}_2$ were chosen for this investigation to test for the contrasting roles of alkalis and alkaline earths on the coordination of TiO_2 in silicate melts.

Additionally, a series of alkali and alkaline earth titanium silicate liquids of $X_{1/n}^{n+}\text{TiSiO}_5$ stoichiometry were chosen to evaluate the effect of exchanges on melt viscosity. Density determinations for all of these liquids are presented in a companion paper (Dingwell, in preparation).

METHOD

The primary joins chosen for this investigation of melt viscosity and the density investigation of Dingwell (in preparation) are the metasilicate- TiO_2 joins, $\text{CaSiO}_3\text{-TiO}_2$ and $\text{Na}_2\text{SiO}_3\text{-TiO}_2$, and melts of the stoichiometry $X_{2/n}^{n+}\text{TiSiO}_5$ (where $X = \text{Ca, Sr, Ba, Li, Na, K, Rb, Cs}$). The starting materials for these viscosity determinations were CaCO_3 (99.5), SrCO_3 , BaCO_3 , Li_2CO_3 , Na_2CO_3 (99.9), K_2CO_3 , Rb_2CO_3 (99), Cs_2CO_3 , TiO_2 (99.8), and SiO_2 (99.5). The starting oxides and carbonates were dried at 120 °C for 24 h prior to weighing. Powder mixtures of the carbonates and oxides were weighed into plastic bottles in batches equivalent to 100 g of decarbonated material. The powders were mixed by agitation for approximately 5 min. The mixed powders were melted stepwise in 75-cm³ Pt crucibles in an MoSi_2 box furnace. The Na-bearing batches were melted at 1150 °C to minimize Na volatilization in these fluid melts, whereas the Ca-bearing batches were melted directly at 1600 °C. The Rb-, Cs-, and K-bearing batches were melted at 1000 °C, whereas the Li-, Ba-, and Sr-bearing batches were melted at 1650 °C. Each melt was poured from the Pt crucible onto a stain-

less steel plate for cooling. The Na-bearing liquids cooled to transparent, colorless glasses, whereas the Ca-bearing liquids cooled to partly crystalline samples. Subsequent X-ray diffraction investigation of the Na-bearing "glass- es" revealed a broad peak indicating poorly crystalline or fine-grained $\text{Na}_2\text{TiSiO}_5$ crystals. Subsequent drop quenches of the $\text{Na}_2\text{TiSiO}_5$ liquid into H_2O yielded glasses with identical X-ray diffraction results. Because of this cryptocrystallinity, no investigations of supercooled liquid viscosity or density were attempted, and the data presented here were obtained at superliquidus temperatures.

After the viscometry experiments, the chemical compositions of glassy fragments of the quenched samples were determined using the electron microprobe. The results and analysis conditions are included in Table 1a. The K, Rb, and Cs glasses were extremely hygroscopic, and the Li melt crystallized fully. Therefore, neither could be analyzed by microprobe. These samples were analyzed using solution-based ICP-AES methods. The results and methods are described in Table 1b. The results (Table 1) confirm the stoichiometric compositions of all the melts.

The shear viscosities of the liquids were determined using the concentric cylinder method at 1 atm in equilibrium with air. The temperature ranges for the Na-bearing and Ca-bearing liquids were 950–1150 °C and 1400–1600 °C, respectively. The viscosities were measured with a Brookfield LVT head (full-scale torque = 6.8×10^{-3} Nt m) and rotation speeds of 50 or 100 rpm. This study used the crucible and low-viscosity spindle design of Dingwell and Virgo (1988). The furnace, viscometer assembly, and computer interface as well as the operating method and calibration are described by Dingwell (1989a, 1990). The viscosities measured are relative. The instrument has been calibrated most recently by standard glass DGG-1 available from the Deutsche Glastechnische Gesellschaft. The viscosity data are accurate to $\pm 5\%$ at 1σ . Newtonian rheology was observed over the limited dynamic range of these measurements (approximately 0.3 \log_{10} units). This result is consistent with the fact that the calculated relaxation times for shear in these liquids using the Maxwell approximation (Dingwell and Webb, 1989, 1990) and the Newtonian viscosity data from this study are several \log_{10} units lower than the experimental strain rates. We appear to be observing relaxed viscosities of a liquid.

After the viscometry was completed, each sample was removed from the furnace, reheated at 1150 or 1600 °C in an MoSi_2 box furnace, and removed quickly from that furnace to be poured once more onto the stainless steel plate. The crucible was cleaned in HF and used for the next sample.

RESULTS AND DISCUSSION

The results of the viscosity determinations are presented in Table 2. The viscosities of all the Na-bearing liquids lie in the range of $\log_{10} \eta = 1.2$ – 0.1 in the 1150–1000 °C temperature range, whereas those of the Ca-bearing liquids lie in the range of $\log_{10} \eta = 0.5$ to -0.5 for the

TABLE 1A. Glass analyses by electron microprobe

Sample	XO/X ₂ O	TiO ₂	SiO ₂	Total
NTS1	46.06 (0.14)**	8.20 (0.17)	45.74 (0.55)	91.89*
NTS2	42.54 (0.10)	15.54 (0.15)	41.93 (0.37)	96.17
NTS3	39.37 (0.20)	23.13 (0.12)	37.50 (0.16)	97.46
NTS4	33.98 (0.16)	32.29 (0.11)	33.73 (0.12)	98.13
NTS5	29.33 (0.10)	40.88 (0.13)	29.78 (0.14)	97.83
CTS1	45.36 (0.21)	7.70 (0.15)	46.94 (0.22)	98.20
CTS2	41.12 (0.10)	16.40 (0.62)	42.49 (0.24)	96.17
CTS3	37.60 (0.30)	22.80 (0.14)	39.61 (0.26)	98.49
CTS4	33.82 (0.17)	30.76 (0.42)	35.38 (0.35)	98.57
CTS5	28.98 (0.13)	40.38 (0.15)	30.66 (0.20)	98.62
CTS6	24.24 (0.09)	50.12 (0.20)	25.65 (0.12)	99.43
STS5	43.08 (0.43)	32.64 (0.20)	24.66 (0.40)	100.38
BTS5	48.48 (0.39)	27.46 (0.45)	22.54 (0.32)	98.48

Note: Microprobe analyses obtained using wavelength dispersive analysis on a Cameca SX 50 instrument. Operating conditions 15 kV accelerating voltage, 15 nA current on brass, a $10 \times 10 \mu\text{m}$ spot, and 20 s counting times. Standards are albite (Na), wollastonite (Ca, Si), and MnTiO_3 (Ti) and synthetic glasses BFS1 (Ba) and SFS1 (Sr). Data are plotted in Figure 1.

* Low total due to H_2O absorption; analyses are averages of ten spots, normalized to 100%.

** Numbers in brackets are 1σ of multiple analyses.

temperature range 1400–1600 °C. The $X_{1/n}^{n+}\text{TiSiO}_5$ liquids range in \log_{10} viscosity from -0.6 to 2.6 . The viscosity-temperature relationships of the liquids are presented in Figures 1a and 1b, and the composition dependence is illustrated in Figures 2a and 2b. The temperature dependence of the viscosity can be described using

$$\log_{10}\eta = a + b/T$$

where a and b are constants. Table 3 contains the values of a and b obtained for these liquids. The temperature dependence of viscosity decreases slightly with increasing TiO_2 content.

The composition dependence of viscosity is plotted as a series of isotherms in Figures 2a and 2b. Viscosity is a

TABLE 1B. Sample analyses by ICP-AES

	XO/X ₂ O	TiO ₂	SiO ₂	Total
LTS5	17.6	47.0(1)	35.9(4)	100.5
NTS5	30.5(5)	39.6(1)	29.2(1)	99.3
KTS5	39.9(1)	34.9(2)	24.8(3)	99.6
RTS5	57(2)	24.7(4)	18.0(1)	99.7
CsTS5	67(4)	19.6(7)	14.4(2)	101.0

Note: Analyses by inductively coupled atomic emission spectroscopy using an HBF₄/HF dissolution of glasses and mixed, single-element standard solutions. Performed on a sequential JY 24 spectrometer from Instruments S.A. Numbers in parantheses represent 1σ .

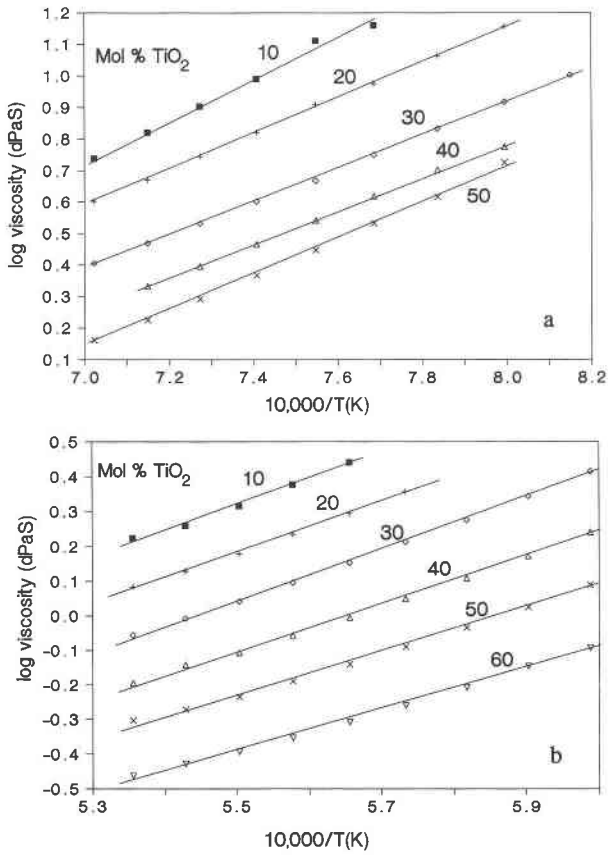


Fig. 1. Viscosity-temperature relationships of liquids on the (a) $\text{Na}_2\text{SiO}_3\text{-TiO}_2$ and (b) $\text{CaSiO}_3\text{-TiO}_2$ joins.

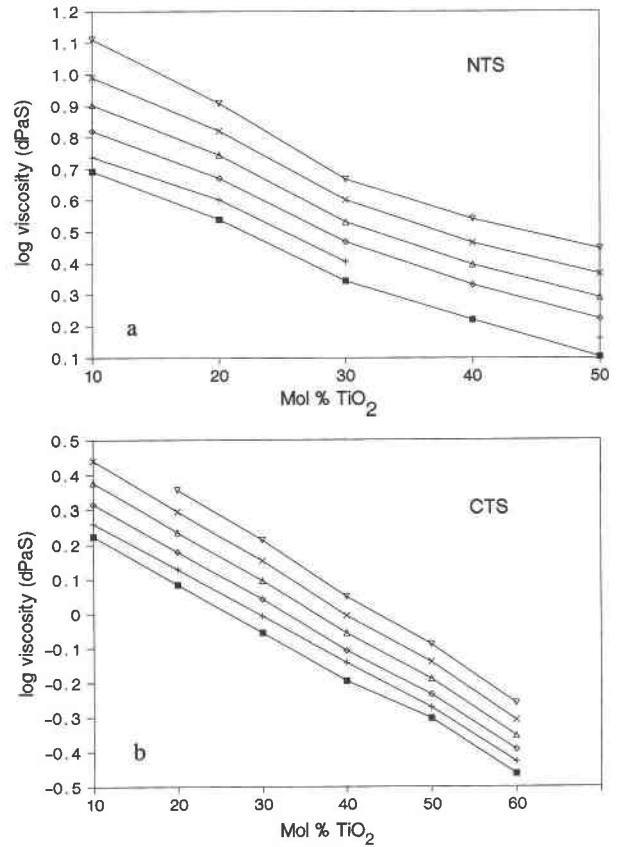


Fig. 2. Viscosity-composition relationships on the (a) $\text{Na}_2\text{SiO}_3\text{-TiO}_2$ and (b) CaSiO_3 joins.

linear function of composition in the $\text{CaSiO}_3\text{-TiO}_2$ system, whereas there is a slight negative deviation from additivity in the $\text{Na}_2\text{SiO}_3\text{-TiO}_2$ system. The $\text{Na}_2\text{SiO}_3\text{-TiO}_2$ data of Figure 1a extrapolate to values in good agreement

with those obtained by Bockris et al. (1955) on Na_2SiO_3 liquid, and the data from the $\text{CaSiO}_3\text{-TiO}_2$ join (Fig. 1b) agree well with the viscosity data of Bockris and Lowe (1954) and Urbain et al. (1982).

TABLE 2A. Viscosity determinations (NTS and CTS)

Temp. (°C)	Viscosity (dPaS)									
	CTS0	CTS1	CTS2	CTS3	CTS4	CTS5	CTS6	CTS7	CTS8	
1594	2.04	1.67	1.21	0.880	0.638	0.497	0.344	0.275	0.223	
1569	—	1.82	1.34	0.983	0.721	0.535	0.373	—	—	
1544	—	2.07	1.51	1.10	0.781	0.583	0.404	0.333	—	
1520	—	2.38	1.72	1.25	0.878	0.647	0.443	—	—	
1495	—	2.76	1.97	1.42	0.987	0.724	0.491	—	—	
1471	—	—	2.27	1.63	1.12	0.814	0.550	—	—	
1446	—	—	—	1.89	1.28	0.924	0.620	—	—	
1421	—	—	—	2.21	1.49	1.06	0.715	—	—	
1397	—	—	—	2.60	1.74	1.23	0.809	—	—	
	NTS1	NTS2	NTS3	NTS4	NTS5					
1151	4.94	3.47	2.21	1.66	1.27					
1126	5.48	4.00	2.55	—	1.45					
1102	6.62	4.70	2.94	2.15	1.68					
1077	8.01	5.56	3.41	2.49	1.96					
1052	9.78	6.61	4.00	2.93	2.33					
1028	12.9	8.10	4.66	3.48	2.80					
1003	14.5	9.45	—	—	—					
978	—	11.6	—	—	—					

Note: Viscosity data are accurate to $\pm 5\%$ at 2σ . Note that these values are in dPaS, not in \log_{10} units.

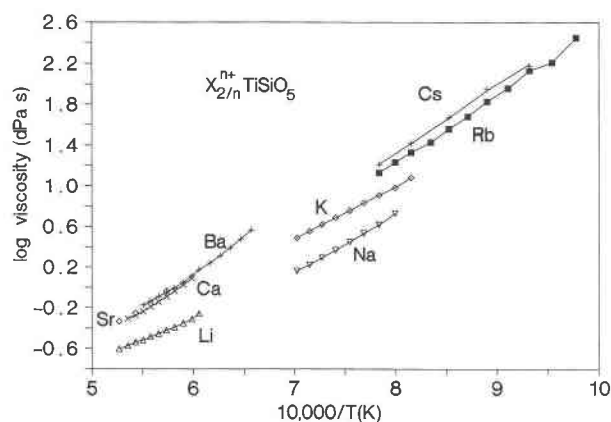


Fig. 3. Viscosity-temperature relationships for melts of the stoichiometry $X_{2/n}^{n+}\text{TiSiO}_5$.

Figure 3 illustrates the viscosity-temperature relationships of the liquids of sphene stoichiometry. The alkaline earth liquids cluster tightly with a slight decrease from $\text{Ba} > \text{Sr} > \text{Ca}$. Similar results have been observed for the alkaline earth galliosilicates (Dingwell, 1990; Balewick and Shelby, 1990), aluminosilicates (Urbain et al., 1982), and ferrosilicates (Dingwell, 1989b). The relative field

TABLE 3. Arrhenius parameters

Sample	a	$b \times 10^3$	Number of data
CTS1	-3.730(0.009)	7.367(0.037)	5
CTS2	-3.805(0.005)	7.249(0.016)	6
CTS3	-4.052(0.006)	7.444(0.010)	9
CTS4	-3.877(0.008)	6.859(0.013)	9
CTS5	-3.678(0.010)	6.270(0.016)	9
CTS6	-3.644(0.010)	5.914(0.015)	9
NTS1	-3.613(0.019)	6.107(0.026)	7
NTS2	-3.307(0.005)	5.472(0.005)	9
NTS3	-3.185(0.005)	5.022(0.004)	10
NTS4	-3.393(0.004)	5.119(0.005)	8
NTS5	-3.762(0.011)	5.485(0.010)	9
CsTS5	-3.983(0.019)	6.343(0.663)	5
RTS5	-4.141(0.030)	6.701(0.124)	11
KTS5	-3.140(0.004)	5.166(0.004)	9
BTS5	-4.031(0.028)	6.948(0.237)	13
STS5	-3.684(0.015)	6.343(0.444)	4
LTS5	-2.841(0.011)	4.233(0.130)	11

Note: Numbers in parentheses are standard errors on the linear regressions. Not to be used for extrapolation of temperature-viscosity relationships.

strengths of the alkaline earth cations have a structural influence on these liquids whose effect for viscosity transcends the identity of the third cation (Ti, Al, Ga, or Fe).

The shear viscosity of the alkali titanates of sphene stoichiometry is more sensitive to cation identity. The

TABLE 2B. Viscosity determinations (XTS5)

Temp. (°C)	Viscosity (dPaS)							
	CsTS5	RTS5	KTS5	NTS5	LTS5	BTS5	STS5	CTS5
1625	—	—	—	—	0.250	—	0.467	—
1594	—	—	—	—	0.268	—	—	0.497
1569	—	—	—	—	0.291	—	0.563	0.535
1544	—	—	—	—	0.304	0.670	—	0.583
1520	—	—	—	—	0.327	0.738	0.695	0.647
1495	—	—	—	—	0.353	0.817	—	0.724
1471	—	—	—	—	0.381	0.901	—	0.814
1446	—	—	—	—	0.407	0.993	—	0.924
1421	—	—	—	—	0.447	1.12	—	1.06
1397	—	—	—	—	0.490	1.30	—	1.23
1378	—	—	—	—	0.559	1.50	—	—
1348	—	—	—	—	—	1.75	—	—
1323	—	—	—	—	—	2.06	—	—
1298	—	—	—	—	—	2.47	—	—
1273	—	—	—	—	—	3.01	—	—
1249	—	—	—	—	—	3.69	—	—
1151	—	—	3.08	1.27	—	—	—	—
1126	—	—	3.58	1.45	—	—	—	—
1102	—	—	4.16	1.68	—	—	—	—
1077	—	—	4.85	1.96	—	—	—	—
1052	—	—	5.70	2.33	—	—	—	—
1028	—	—	6.78	2.80	—	—	—	—
1003	16.2	13.5	8.11	—	—	—	—	—
978	26.3	17.0	9.59	—	—	—	—	—
954	46.8	21.4	12.0	—	—	—	—	—
925	89.1	26.9	—	—	—	—	—	—
900	151	36.3	—	—	—	—	—	—
875	—	47.9	—	—	—	—	—	—
850	—	67.6	—	—	—	—	—	—
825	—	91.2	—	—	—	—	—	—
800	—	135	—	—	—	—	—	—
775	—	170	—	—	—	—	—	—
750	—	282	—	—	—	—	—	—

Note: Viscosity data are accurate to $\pm 5\%$ at 2σ . Note that these values are in dPaS, not in \log_{10} units.

viscosity decreases 0.6 \log_{10} units with alkali substitution from Cs to Na. Data for the Li composition are insufficient to distinguish the trend further. The general behavior of the alkali titanosilicates matches again that of the equivalent gallio-, aluminio-, and ferrosilicate liquids.

One apparent contrast to the trends observed for gallio-, ferro-, and aluminosilicate liquids is the observation that the alkali titanium silicates have lower viscosities than the alkaline earth titanium silicate liquids. In a companion study, the densities of all of the investigated liquids have been determined (Dingwell, in preparation). The partial molar volume of TiO_2 has been computed for each of the liquids of sphene stoichiometry. The partial molar volume of TiO_2 is alkali-cation specific. In general, much larger values are observed for the alkali vs. the alkaline earth titanium silicates and pure TiO_2 liquid (Dingwell, 1991), suggesting that Ti has a lower coordination number in the alkali titanium silicates. The apparent shift in coordination number of Ti in the alkali titanium silicate liquids may be responsible for the lower viscosity observed for the alkali silicate vs. the alkaline earth silicate liquids.

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