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Anomalous rheology of peraluminous melts

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ABSTRACT

The viscosity of peraluminous Na_2O-Al_2O_3-SiO_2 melts of constant SiO_2 content is essentially independent of Al_2O_3 content. The addition of more Al^{3+} to the peraluminous melts does not result in a decrease in viscosity. This finding indicates that the Al^{3+} in these melts does not enter the structure as a viscosity reducing network-modifier. The most probable charge-balanced structural unit in these melts is a tri-cluster that involves one Al-tetrahedron sharing an O atom with two Si-tetrahedra. Both viscosity and activation energy for viscous flow in the investigated viscosity range in these peraluminous melts are largely unaffected by the Al^{3+} content, indicating that increasing the proportion of tri-clusters does not significantly affect the mechanism of viscous flow. Comparison of data for melts of different SiO_2 contents shows that the viscosity of melts in the Na_2O-Al_2O_3-SiO_2 system form the same trend ±1 $\log_{10}$ unit as a function of Na:Al ratio within the 10^8–10^{14} Pa·s range.

INTRODUCTION

The structure of peraluminous composition melts has yet to be understood fully. The Na_2O-Al_2O_3-SiO_2 system is widely used as an analog for more complex magmas. The structure of melts in this system is assumed to be made up of network-forming tetrahedrally co-ordinated Si^{4+} atoms and network-forming tetrahedrally co-ordinated Al^{3+} atoms that are charge-balanced by Na^+, with the remaining Na^+ acting as network modifiers—that is, these atoms terminate a network in that they have one bond to an O atom (Mysen 1987). This description pertains to peralkaline compositions (Na/Al>1). If the melt composition is changed by decreasing the number of Na^+ ions, there comes a stage where all of the Na^+ are used to charge balance the tetrahedrally co-ordinated Al^{3+}. At this subaluminous join (Na/Al = 1), the network should be fully polymerized, based upon the above structural model. With a further decrease in the amount of Na^+, the question is what happens to the structure of the melt and its rheology? The two extremes of structure available to the "excess" Al (that which has no Na^+ to charge-balance it in tetrahedral co-ordination) are that it acts as a network-modifier in octahedral co-ordination (Mysen et al. 1981; Mysen 1988), or that it continues to occur as a tetrahedrally co-ordinated network-former in the form of "tri-clusters" (Lacy 1963) in which one O atom is the apex of two Si^{4+} tetrahedra and one Al^{3+} tetrahedron. This Na-free tri-cluster is a charge-balanced fully polymerized structural unit.

Within the framework of this structural model, it is expected that there is a maximum in viscosity for melts of constant mol% SiO_2 at Na/Al = 1, as this composition is the point of maximum average bond strength and minimum configurational entropy of the melt (Toplis et al. 1997a). This is the composition at which all of the network-modifying Na atoms are used to charge-balance the Al-tetrahedra. On the peralkaline side of this composition, there is an increasing number of network-modifying Na^+, and on the peraluminous (Na/Al<1) side, there are increasing amounts of either network-modifying Al^{3+} or some other structural unit that results in the charge balance of the tetrahedrally co-ordinated Al^{3+} cations. The changes in viscosity that result from the necessary changes in structure as a function of Na:Al have been observed by several authors. The data of Riebling (1966, 1968) show a maximum in viscosity (in the range 10^1–10^2 Pa s) for $0.45<Na_2O/(Na_2O + Al_2O_3)<0.50$ for melts of constant SiO_2 content in the range 50–75 mol% SiO_2. Taylor and Rindone (1970) found in the 10^9–10^{13} Pa s range that viscosity increased with decreasing peralkalinity and then remained essentially constant with increasing peraluminosity for melts with 75 mol% SiO_2. Hunold and Brückner (1980) combined rotation viscometry with micro-penetration techniques and investigated the viscosity of melts with 66.7 mol% SiO_2 across the 10^1–10^{13} Pa·s range and found a shallow maximum occurring for Al-rich melts at $Na_2O/(Na_2O + Al_2O_3) \sim 0.45$. The maximum was more pronounced for the high viscosity measurements (see Fig. 1).

More recently, Toplis et al. (1997a, 1997b) determined the viscosity of several Na_2O-Al_2O_3-SiO_2 melts with $SiO_2 \geq 50$ mol%, and observed the maximum in viscosity to occur in the slightly peraluminous compositions. They found the Na:Al ratio at which the maximum in viscosity occurs to be dependent upon the SiO_2 content, and also upon temperature. Toplis et al. (1997a) interpreted their results to be consistent with a melt structure containing a proportion of tri-clusters in which one three-coordinated O atom shares an aluminate and two silicate tetrahedra. The existence of this charge balanced tri-cluster results in the presence of non-bridging O atoms bonded to Na^+ in slightly peraluminous compositions (as observed in NMR studies; e.g., Stebbins and Xu 1997; Stebbins et al. 2001). The presence of octhedrally co-ordinated Al^{3+} acting as network-modifying cations would also result in a decrease in viscosity with increasing peraluminosity, and thus also explain the maximum observed in viscosity at Na/Al~1. However, as pointed out by Toplis et al. (1997a), the maximum in viscosity occurs for the most peraluminous composition at 67 mol% SiO_2, and the clusters of four Al^{3+} required when one Al^{3+} acts as a charge

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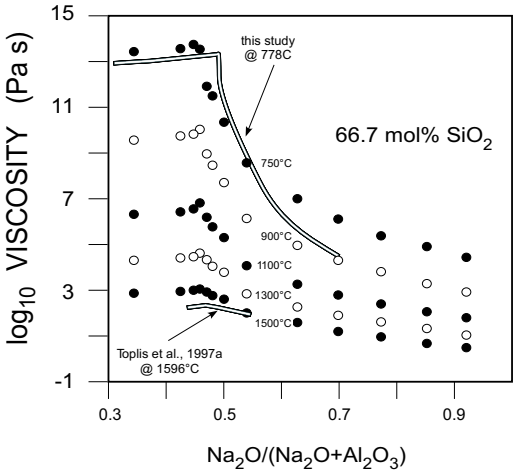

FIGURE 1. Viscosity data for Na_2O-Al_2O_3-SiO_2 melts (with 66.7 mol% SiO_2) from Hunold and Brückner (1980) plotted as a function of $Na_2O/(Na_2O + Al_2O_3)$ for temperatures from 750 to 1500 °C, together with the trend of the present data at 778 °C, and the trend of the viscosity data of Toplis et al. (1997a) at 1596 °C.

TABLE 1. Glass compositions (mol%) determined by microprobe (JEOL JXA 8900 RL): 15 kV voltage, 10 µm beam diameter, and 12 nA current

	SiO_2	Na_2O	Al_2O_3	Wt% total	Na_2O / ($Na_2O + Al_2O_3$)	Na_2O wt% AAS
67:36	68.52±0.41 (58.51)	11.37±0.49 (10.01)	20.11±0.17 (29.14)	97.64	36.1±1.1	9.36±0.06
67:40.3	68.23±0.31 (58.70)	12.82±0.30 (11.38)	18.95±0.20 (27.67)	97.74	40.3±0.7	10.83±0.05
67:40.4	66.85±0.23 58.10	13.39±0.12 12.00	19.76±0.11 29.14	99.24	40.4±0.1	11.74±0.07
67:47	67.64±0.27 (59.10)	15.31±0.25 (13.80)	17.05±0.13 (25.28)	98.17	47.3±0.5	14.40±0.06
67:48	67.19±0.26 (58.89)	15.95±0.28 (14.42)	16.86±0.15 (25.07)	97.38	48.6±0.4	15.17±0.05
67:49	64.97±0.17 (56.22)	17.19±0.16 (15.34)	17.84±0.17 (26.20)	97.75	49.1±0.4	15.01±0.11
67:51	66.70±0.28 (58.69)	16.95±0.38 (15.39)	16.35±0.18 (24.41)	98.48	50.9±0.8	16.21±0.05
67:58	69.93±0.56 63.32	17.38±0.36 16.24	12.69±0.22 19.52	99.07	57.8±0.2	18.20±0.13
67:59	67.52±0.97 (60.54)	19.30±1.14 (17.85)	13.18±0.24 (20.05)	98.44	59.4±2.0	18.55±0.06
67:70	67.28±0.19 62.16	22.93±0.17 21.85	9.79±0.04 15.36	99.38	70.1±0.1	22.48±0.06

Notes: Data are the average of 10 analyses of each glass. Errors are 1σ values. The numbers in brackets are the wt% values. The $Na_2O/(Na_2O + Al_2O_3)$ values calculated from the microprobe data are in percentages. The Na_2O determined by atomic absorption spectroscopy are also given in wt%.

balancer for the other three would not result in this maximum deviation at 67 mol% SiO_2. Therefore it appears that the structure of peraluminous composition melts contains $AlSi_2O_{5.5}$ tri-clusters rather than octahedrally co-ordinated Al^{3+}. As pointed out by Toplis et al. (1997a), their data cannot, however, be used to infer the presence or absence of octahedral Al in more highly peraluminous compositions.

To address the further possible changes in melt structure with increasing alumina content, the viscosity of several Al_2O_3- and also Na_2O-rich melts with 66.7 mol% SiO_2 content were determined by the micro-penetration technique.

EXPERIMENTAL METHODS

Ten samples were made from Na_2CO_3, Al_2O_3 and SiO_2 powders. The powdered mixtures were homogenized by agitation in plastic bottles, de-carbonated in Pt-crucibles at 700 °C for 12 hours, and melted at temperatures between 1250 and 1600 °C. The Na-rich samples were melted at the lower temperatures. The peraluminous melts were stirred with a Pt-stirrer at 1600 °C for 12 hours to remove the bubbles. The melts were cooled slowly (2 °C/min) through the interval between 900 and 600 °C to minimize thermal stresses. The bubble-free samples were then cored out of the crucible with a diamond borer and 3 mm thick, 8 mm diameter discs were cut for the viscosity measurements. The parallel faces of the discs were polished before the viscosity measurements. The compositions of the ten glasses (see Table 1) were determined by electron microprobe analysis. The samples were found to be crystal-free based on both optical microscopy and the surfaces observed during the microprobe measurements.

The micropenetration technique was used to determine viscosity in the range 10^8–$10^{14.5}$ Pa·s. Shear viscosities for several silicate melt compositions have been determined in previous studies using the micro-penetration technique (e.g., Douglas et al. 1965; Brückner, and Demharter 1975). Viscosity was measured with a Netzsch TMA 402 Dilatometer. The rate at which a 2 mm diameter single crystal sphere of Al_2O_3 is forced into the melt is measured, and viscosity is calculated by:

$$\eta = \frac{0.1875\ F\ t}{r^{0.5}\ l^{1.5}} \quad (1)$$

for F = the applied force, t = time, r = radius of the sphere and l = indent distance. A typical plot of calculated viscosity as a function of time is shown in Figure 2. Masses between 50 and 500 g were used to apply the force for indent times from 15 minutes to 12 hours. The sample temperature within the dilatometer was calibrated to within ±0.5 °C from the melting points of Ag (961.8 °C), Al (660.3 °C), Sb (630.6 °C) and Zn (419.5 °C) determined for heating rates from 1 to 10 °C/min. The viscosity of the standard glass DDG1 from the Deutsche Glastechnische Gesellschaft was determined to within 0.05 $\log_{10}$ Pa s or better for viscosities between $10^{9.2}$ and $10^{12.5}$ Pa·s. The viscosity was also shown to be independent of the force applied, with the same viscosity (within ±0.02 $\log_{10}$ Pa·s) being determined for forces of 0.2 to 4.5 N. Based upon the precision and accuracy of these calibrations, 1σ error of 0.06 $\log_{10}$ Pa·s is assigned to each viscosity determination. As these melts are highly viscous, some of the data were collected over a 12 hour period with the unrelaxed penetration data being discarded. In general, relaxed penetration data were obtained 3τ after the application of the load, where τ is the relaxation time calculated from the Maxwell equation [τ = (viscosity)/(elastic shear modulus)].

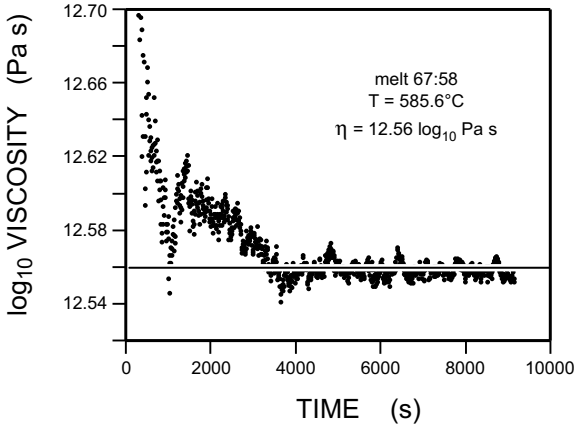

FIGURE 2. Viscosity calculated as a function of time for melt 67:58, for an applied force of 1.303 N. The black line is the fit to the data.

RESULTS

The measured viscosities as a function of temperature are in Table 2 and Figure 3. The error in each viscosity determination is ±0.06 $\log_{10}$ Pa·s. Over the ~200 °C temperature range of the

TABLE 2. The $\log_{10}$ viscosity measured at each temperature

67:36		67:40.3		67:40.4		67:47		67:48	
T (°C)	$\log_{10}\eta$ (Pa s)	*T* (°C)	$\log_{10}\eta$ (Pa s)	*T* (°C)	$\log_{10}\eta$ (Pa s)	*T* (°C)	$\log_{10}\eta$ (Pa s)	*T* (°C)	$\log_{10}\eta$ (Pa s)
746.2	13.84	773.0	13.17	799.7	12.43	762.5	13.63	762.5	13.67
772.8	13.17	834.7	11.61	834.7	11.61	781.1	13.20	803.8	12.68
830.6	11.65	870.7	10.72	886.2	10.42	803.8	12.57	839.8	11.73
868.7	10.71	906.8	9.89	906.8	9.93	844.9	11.42	877.8	10.74
906.8	9.83	947.8	9.04	927.3	9.47	881.0	10.64	906.8	10.11
989.0	8.31	989.0	8.36	937.6	9.21	906.8	10.07	968.5	8.90
				974.6	8.42	947.8	9.32		
						989.1	8.57		

67:49		67:51		67:58		67:59		67:70	
T (°C)	$\log_{10}\eta$ (Pa s)	*T* (°C)	$\log_{10}\eta$ (Pa s)	*T* (°C)	$\log_{10}\eta$ (Pa s)	*T* (°C)	$\log_{10}\eta$ (Pa s)	*T* (°C)	$\log_{10}\eta$ (Pa s)
773.0	13.56	711.2	12.82	585.6	12.56	553.7	13.71	476.1	14.47
809.0	12.55	752.3	11.76	585.6	12.61	564.0	13.38	500.4	13.30
839.8	11.70	793.4	10.80	618.6	11.40	587.7	12.31	529.9	11.95
881.0	10.69	829.5	10.02	639.1	10.75	602.1	11.86	563.0	10.90
906.8	10.06	868.7	9.26	650.5	10.40	618.0	11.05	587.2	9.88
958.1	8.99	901.6	8.67	660.8	10.11	643.3	10.36	617.7	8.93
				670.0	9.80	673.0	9.51	637.9	8.49
				680.3	9.51	706.0	8.86		
				690.6	9.26				
				700.9	9.01				
				711.2	8.78				

Notes: The 1σ error in viscosity is ±0.06 $\log_{10}$ Pa s. The melt compositions are indicated by the $Na_2O/(Na_2O + Al_2O_3)$ value.

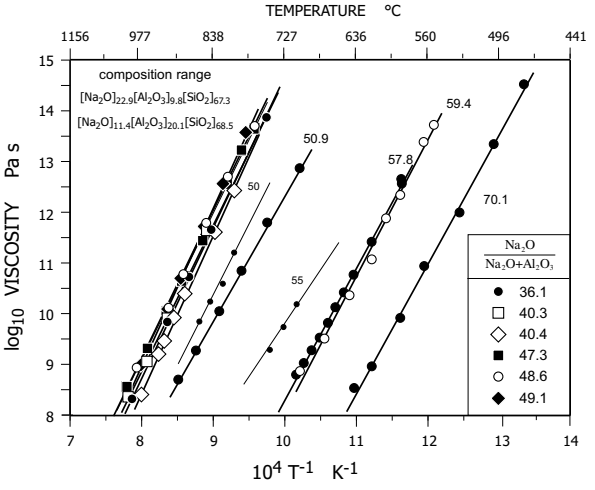

FIGURE 3. Viscosity of Na_2O-Al_2O_3-SiO_2 melts as a function of inverse temperature. The 1σ error in viscosity is less than the size of the symbols. The small dots are the data from Toplis et al. (1997a) for their melts 67:50 and 67:55. The $Na_2O/(Na_2O + Al_2O_3)$ values are determined from the microprobe data.

present measurements, the data in Figure 3 are best fit by an Arrhenius equation:

$$\log_{10}\ \eta\ (\text{Pa s}) = A + \frac{B\times 10^4}{T} \qquad (2)$$

with the resulting parameters and their standard deviation presented in Table 3. Arrhenian fits to the micropenetration viscosity data of Toplis et al. (1997a, 1997b) were calculated to compare their data with that of the present study. These fit parameters are also included in Table 3. There are large errors in the activation energy term determined from the data of Toplis et al. (1997a, 1997b) as they have four or fewer data points in this high viscosity range. There appears to be a general trend that the activation energy is larger for the peraluminous compositions. As can be seen in Figure 3, the viscosity of peralkaline composition melts increases with increasing Al_2O_3 content for $0.50 < Na_2O/(Na_2O+Al_2O_3) < 0.70$. However, once the melt becomes peraluminous, the viscosity appears not to change—despite the addition of more Al_2O_3 for melts with $0.36 < Na_2O/(Na_2O + Al_2O_3) < 0.49$.

TABLE 3. Parameters fit to Equation 2 together with the activation energy for viscous flow for each composition.

Melt	$\frac{Na_2O}{Na_2O + Al_2O_3}$	A-value ($\log_{10}$ Pa s)	B-value (K)	Activation energy (kJ mol^{-1})
67:36	0.361	−15.86 ± 0.22	3.03 ± 0.02	581 ± 5
67:40.3	0.403	−15.29 ± 0.33	2.98 ± 0.04	570 ± 7
67:40.4	0.404	−16.13 ± 0.41	3.07 ± 0.05	588 ± 10
67:44[Ta]	0.441	−19.44 ± 4.82	3.43 ± 0.55	657 ±106
67:47[Tb]	0.470	−19.78 ± 3.62	3.50 ± 0.42	669 ± 80
67:47	0.473	−14.97 ± 0.38	2.96 ± 0.04	567 ± 8
67:48	0.486	−15.51 ± 0.43	3.03 ± 0.05	580 ± 9
67:49	0.491	−16.96 ± 0.18	3.19 ± 0.02	611 ± 4
67:50[Tb]	0.492	−14.54 ± 2.30	2.76 ± 0.25	529 ± 49
67:51	0.509	−12.83 ± 0.17	2.52 ± 0.02	483 ± 3
67:55[Tb]	0.548	−14.30 ± 0.89	2.41 ± 0.09	461 ± 17
67:58	0.578	−17.61 ± 0.30	2.59 ± 0.03	496 ± 6
67:59	0.594	−18.56 ± 1.07	2.66 ± 0.09	509 ± 18
67:70	0.701	−19.54 ± 0.67	2.54 ± 0.05	486 ± 10

Notes: The errors are the standard deviation to the fit parameters. Ta = data from Toplis et al. 1997a; Tb = data from Toplis et al. 1997b.

DISCUSSION

To address the variation in viscosity as a function of melt structure and Na:Al value, the present viscosity data are plotted at 778 °C as a function of $Na_2O/(Na_2O + Al_2O_3)$ in Figure 4. The viscosity data of Toplis et al. (1997a) at this temperature are also included in Figure 4. For seven of the present melts, this plot requires no extrapolation beyond the measured temperature range. For the three Na_2O-rich samples, this plot requires a 70 to 140 °C extrapolation in temperature, which is equivalent to a ~4 $\log_{10}$ unit extrapolation in viscosity. Using the data from Toplis et

al. (1997a) for their melt 67:55, it is found that such an Arrhenian extrapolation will underestimate the actual viscosity by 1 $\log_{10}$ Pa s. Extrapolation of the Arrhenian fit to the present data for melt 67:70 to 750 °C underestimates the viscosity measured by Hunold and Brückner (1980) by 0.8 $\log_{10}$ Pa s; while extrapolations of the Arrhenian curve for melts 67:58 and 67:59 plot within error of the Hunold and Brückner data at 750 °C.

The general trend in viscosity data observed in Figure 4 is essentially independent of temperature: the viscosity of the peralkaline melts is low and increases as the Na = Al join is approached, and then remains essentially unchanged as the melts become more peraluminous. As pointed out by Hunold and Brückner (1980) and Toplis et al. (1997a, 1997b), the difference in viscosity as a function of composition is minimal at high temperatures, and more extreme at the low-temperature, high-viscosity conditions of this study (see Fig. 1). The data in Figure 4 show a weak maximum in viscosity at $Na_2O/(Na_2O + Al_2O_3) \sim 0.49$. As observed by Toplis et al. (1997a), this maximum occurs on the peraluminous side of the composition range, which they interpreted to indicate the presence of tri-clusters in the melt structure in the vicinity of the subaluminous join. Figure 4 shows there is a plateau (±1 $\log_{10}$ Pa·s) in viscosity with increasing peraluminosity. The occurrence of this plateau indicates that Al^{3+} does not exist in these peraluminous melts in a network-modifying role, as this would result in a decrease in viscosity similar to that observed for increasingly peralkaline melts. In contrast to the study of Toplis et al. (1997a), in which the maximum in viscosity as a function of composition was determined from a 0.6 $\log_{10}$ Pa·s change in viscosity, the present study is concerned with large changes in viscosity. The ±1 $\log_{10}$ Pa·s variation for the peraluminous compositions appears as a "constant" viscosity, in comparison to the ~8 $\log_{10}$ Pa·s change in viscosity occurring for the peralkaline compositions (see Fig. 4).

The current perception of melt structure is based upon tetrahedrally bonded Si^{4+}, and tetrahedrally bonded Al^{3+} charge-balanced by an Na^+, with the excess Na^+ in peralkaline compositions bonded to non-bridging O atoms (Lacy 1963; Mysen 1988). This model, however, breaks down when there is more Al^{3+} than charge-balancing cations, that is, for peraluminous compositions. Peraluminous melts require a different structure model. One possibility is that Al^{3+} becomes a network modifier, which would result in a decrease in viscosity for peraluminous melts with increasing amounts of alumina. However, the present data, as well as the low-viscosity data of Riebling (1966, 1968) and the high- and low-viscosity data of Hunold and Brückner (1980), show no decrease in viscosity with increasing Al-content in peraluminous composition melts. The relatively constant, composition-independent viscosity for the peraluminous melts indicates that there are no new non-bridging O atoms being created in the structure as the melt becomes more Al rich. This "constant" viscosity also would suggest that the average bond strength and configurational entropy of the melt does not change appreciably as the melt composition becomes more Al rich (Toplis et al. 1997a).

Lacy (1963) and Toplis et al. (1997a) (as well as many others) discussed the possible structure of peraluminous melts and concluded that tri-clusters of one Al-tetrahedron and two Si-tetrahedra all sharing one O atom are the most probable structure in slightly peraluminous melts. Such a tri-cluster is charge-balanced. Toplis et al. (1997a) pointed out that the existence of the local maximum in viscosity on the peraluminous side of the composition range supports the existence of $AlSi_2O_{5.5}$ tri-clusters. The chemically induced creation of a tri-cluster does not require the polymerization (time average of the number of bridging and non-bridging O atoms) of the melt to change. The removal of one Na_2O from a fully polymerized peraluminous melt results in the creation of two tri-clusters; but no new non-bridging O atoms are required. Similar scenarios in which the polymerization remains unaffected and tri-clusters are formed can be developed for the combined removal of a $NaO_{0.5}$ and addition of an $AlO_{1.5}$, or the simple addition of one Al_2O_3.

Figure 5 shows the viscosity of a range of Na_2O-Al_2O_3-SiO_2 melts with $50 \le SiO_2$ mol% ≤ 82 at 778 °C. All of these data fall within ±1 $\log_{10}$ unit of the same trend seen in Figure 4. Thus, in this simple ternary system, the viscosity can be estimated within ±1 $\log_{10}$ Pa·s in terms of the Na_2O:Al_2O_3 ratio, independent of the SiO_2 content. Trends similar to that of Figure 4 can be calculated

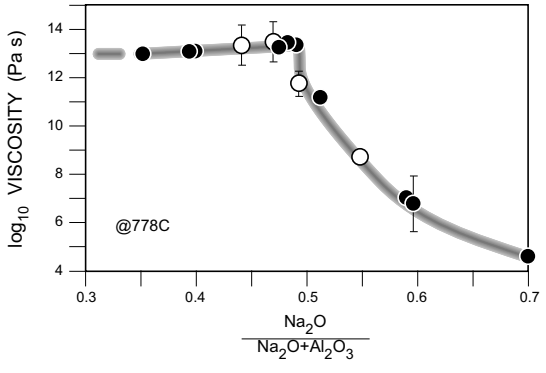

FIGURE 4. Viscosity data at 778 °C = filled symbols. The open symbols are the viscosity calculated at this temperature from Arrhenian fits to the micropenetration data of Toplis et al. (1997a). Unless otherwise indicated, the error in viscosity is less than the size of the symbol. The grey curve is a guide to the eye.

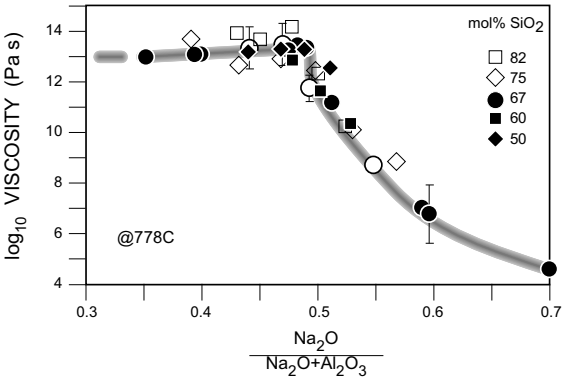

FIGURE 5. Viscosity of a range of Na_2O-Al_2O_3-SiO_2 melts with varying SiO_2 content at 778 °C; solid circles = present data; all other symbols are data from Toplis et al. (1997a, 1997b). They grey curve is the same as drawn in Figure 4.

for other temperatures, which, however, involves extrapolation of several sets of viscosity data beyond the 10^8–$10^{14.5}$ Pa·s range that is described by the present Arrhenian fits. This procedure would involve increasingly larger errors in the extrapolated viscosities. Figure 6 illustrates that Na-aluminosilicate melts with $50 \le SiO_2$ mol% ≤ 82, and $Na_2O = Al_2O_3$ have viscosities within ± 1 $\log_{10}$ Pa·s of that for the jadeite composition at all temperatures. Figure 7 illustrates the same set of viscosity data together with other literature data now plotted as a function of NBO/T. The NBO/T is calculated from:

$$\frac{NBO}{T} = \frac{2(Na_2O\text{-}Al_2O_3)}{2Al_2O_3+SiO_2} \quad (3)$$

assuming no tri-clusters exist, where the components are in mole fractions of the oxides (Mysen 1987). For the melt compositions that do not have enough Na^+ to charge-balance the Al^{3+}, which are assumed to be in tetrahedral coordination, this calculation gives negative NBO/T values. If tri-clusters, or some other structure that does not create non-bridging O atoms exist in these peraluminous melts, the negative NBO/T values would become equal to zero. The data in Figures 5 and 7 suggest that viscosity of Na_2O-$Al_2O_3SiO_2$ melts is a simple function of the degree of polymerisation of the melt structure. The Arrhenian activation energy for viscous flow at 10^{12} Pa·s in the present Na_2O-Al_2O_3-SiO_2 melts with 67 mol% SiO_2 is plotted as a function of $Na_2O/(Na_2O + Al_2O_3)$ in Figure 8. There appears to be a general trend of low activation energy (~480 kJ/mol) for Na>Al, and high activation energy (~560 kJ/mol) for viscous flow for Al>Na. Although there are large errors (± 50 kJ/mol) in activation energy from the literature, based upon the low-temperature viscosity data of Poole and Gensamer (1949), Taylor and Rindone (1970), and Toplis et al. (1997a, 1997b), the activation energy also appears to be independent of SiO_2 content. A similar trend in activation energy as a function of composition is seen in the data of Riebling (1966, 1968) for the low-viscosity range for melts with $50 < SiO_2$ mol% < 75.

Toplis (1998) showed that within the framework of the Adam-Gibbs theory of viscosity, the ratio of the parameters B_e (temperature independent constant) to $S_c(T_g)$ (configurational entropy at the temperature where viscosity is 10^{12} Pa·s) is proportional to the height of the average potential energy barrier to viscous flow (assuming the size of the rearranging structural domains at this temperature is a constant for all silicate melt compositions). The term $B_e/S_c(T_g)$ is linearly proportional to the activation energy term calculated for the present melts using the Arrhenius equation. The constant value of activation energy for the present peraluminous melts (see Fig. 8) would suggest, therefore, that the mechanism of viscous flow in these melts

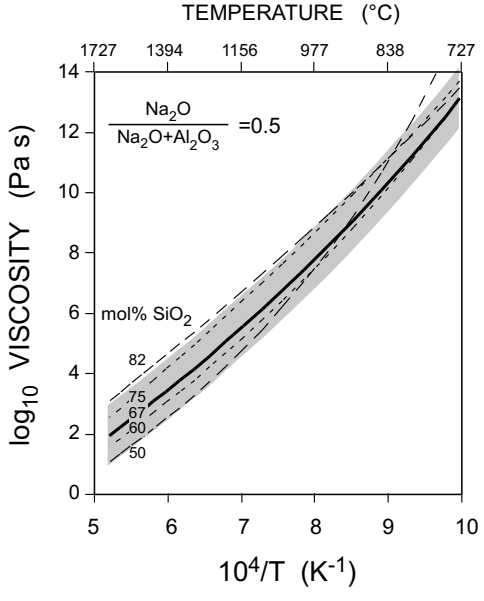

FIGURE 6. The viscosity of Na_2O-Al_2O_3-SiO_2 melts with Na = Al. Data from Toplis et al. (1997a, 1997b). The shaded area indicates ± 1 $\log_{10}$ Pa s centred on the viscosity of the melt with 67 mol% SiO_2.

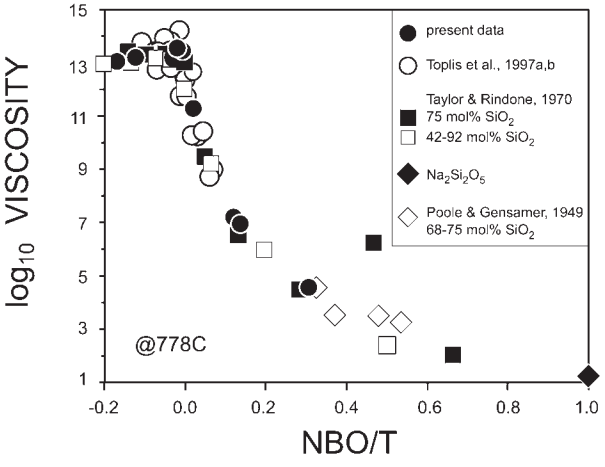

FIGURE 7. Viscosity of a range of Na_2O-Al_2O_3-SiO_2 melts at 778 °C as a function of NBO/*T*. In this case, negative values of non-bridging O atoms are calculated to illustrate the need for a change in melt structure. Data that plot below 10^8 Pa·s involve the extrapolation of Arrhenian fits to high-viscosity data and are thus increasingly larger (>1 $\log_{10}$ unit) underestimates of the real viscosity.

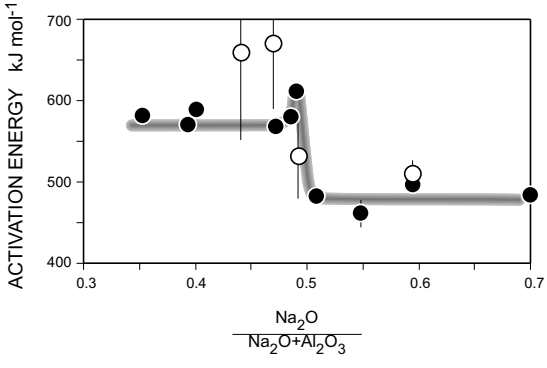

FIGURE 8. Activation energy from Arrhenian fits to the viscosity data. Unless otherwise indicated, the 1σ errors are less than the size of the symbols. The open symbols are from fits to the data of Toplis et al. (1997a, 1997b). There are large errors in these energy values as only three or four data exist at these low temperatures.

does not change with increasing amounts of Al^{3+}, nor with the increasing proportions of the structure that Al^{3+} takes up in these peraluminous compositions. Similarly it can be argued that the constant activation energy for the peralkaline melts with 67 mol% SiO_2 indicates that the mechanism of viscous flow is unaffected by increasing amounts of non-bridging O atoms that accompany an increase in Na^+ content. The jump from low activation energy for viscous flow in peralkaline melts to higher activation energies in peraluminous melts would, however, suggest that the mechanism of viscous flow between the two compositions changes from (1) a mechanism in which weak O-Na bonds are broken in order for flow to occur in peralkaline melts to (2) a mechanism in which stronger O-Al bonds need to be broken for flow to occur in peraluminous melts (McMillan et al. 1994; Stebbins 1995; Toplis 1998).

The trend in viscosity with Na_2O:Al_2O_3 ratio has not been appreciated previously, as most geological systems have a more complex chemistry. As shown in Figure 9, a similar trend may occur in mixed alkali melts. A very different pattern of viscosity as a function of composition (and NBO/T) appears for the alkaline earth compositions. There is limited data for these compositions in the peraluminous range and therefore it is not possible to determine whether there is also a plateau in viscosity for the peraluminous alkaline earth compositions.

Concluding remarks

Viscosity measurements for a wide range of Na_2O-Al_2O_3-SiO_2 composition melts shows that there is not a maximum in viscosity in the vicinity of the Na = Al composition, rather, there is a plateau in viscosity for peraluminous melts. Thus, the Al^{3+} replacing Na^+ in the peraluminous composition melts do not enter the melt structure as viscosity reducing network modifiers, or as structures that result in the formation of more non-bridging O atoms. The most probable peraluminous melt structure is that discussed by Lacy (1963) and Toplis et al. (1997a, 1997b), in which tri-clusters of one O atom shared by two Si-tetrahedra and one Al-tetrahedron exist. This structural unit is charge-balanced and does not reduce the polymerization of the melt. The lack of change in viscosity with increasing Al-content together with the relatively constant activation energy for viscous flow with respect to that for the $16.7Na_2O{\cdot}16.7Al_2O_3{\cdot}66.7SiO_2$ composition suggests that the presence of an increasing number of tri-clusters does not affect the mechanism of flow in these melts.

Figure 4 also illustrates the reason for the different glass transition temperatures and viscosities for different "albite" compositions observed by Knoche et al. (1992). They observed a 100 °C decrease in T_g for albite composition melts with $Na_2O/(Na_2O + Al_2O_3)$ of 48.8 and 51.8. The viscosity in Figure 4 is seen to decrease rapidly for slightly Na-rich compositions, but remain essentially constant for the Al-rich melts in the vicinity of the 1:1 join for Na and Al. The viscosity decrease from $Na_2O/(Na_2O + Al_2O_3) = 0.49$ to 0.52 is approximately 2.5 $\log_{10}$ Pa·s, which is equivalent to a 100 °C change in temperature (see Table 2).

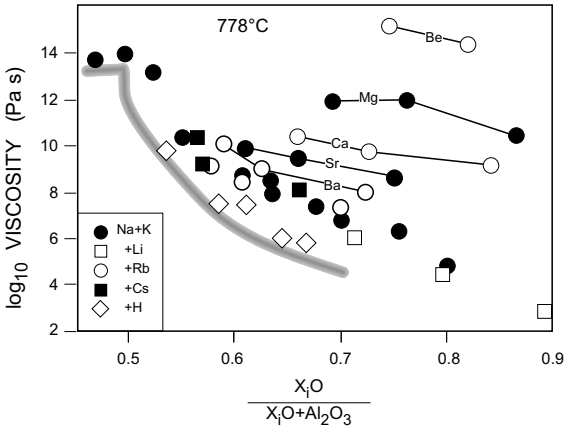

Figure 9. Viscosity of granitic composition melts at 778 °C as a function of alkali and alkaline earth content. The HPG8 composition (solid circles) has various amounts of H_2O, Li_2O, Rb_2O, Cs_2O, BeO, MgO, CaO, SrO, and BaO added to it. The grey curve is that of Figure 4. Data from Hess et al. (1995, 1996) and Dingwell et al. (1996).

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