

## Viscosity regimes of homogeneous silicate melts

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### ABSTRACT

Extrapolation of laboratory measurements of the viscosity ( $\eta$ ) of silicate melts is frequently needed in order to analyze petrological and volcanological processes. Therefore a general understanding of silicate melt viscosities is required. In this paper we survey the present state of our knowledge and distinguish three flow regimes for homogeneous silicate liquids: (1) a low-viscosity regime ( $\eta < 1 \text{ Pa}\cdot\text{s}$ ), where the viscosity obeys a temperature-dependence power law in accordance with mode coupling theory (these low viscosities are typical for depolymerized melts); (2) an intermediate regime ( $1 < \eta < 10^{12} \text{ Pa}\cdot\text{s}$ ), where silicate melt viscosity is determined by the availability of configurational states (the dependence of the viscosity on the temperature is described aptly by the configurational entropy theory of Adam-Gibbs); and (3) a high-viscosity regime, where the liquid has been transformed into a glass ( $\eta > 10^{12} \text{ Pa}\cdot\text{s}$ ) (this regime is not well known, but available measurements indicate an Adam-Gibbs or an Arrhenian temperature dependence of the glass viscosity). Examples are given of igneous rocks whose geneses were affected by these flow regimes.

### INTRODUCTION

The viscosity of bubble- and crystal-free silicate melts is an important parameter in the modeling of igneous petrological and volcanological processes. This parameter informs us about the flow properties and the structural relaxation time of the melt. In nature, the viscosity of silicate melts can vary over an interval of more than ten orders of magnitude, depending on the temperature, pressure, and chemical composition of the melt. Most of our knowledge of silicate melt viscosities is for temperatures of 1200 °C and higher, a pressure of 1 atm, and simple melt compositions free of dissolved volatiles. But low-pressure petrological and volcanological processes of interest to Earth scientists take place at temperatures much lower than 1200 °C, whereas the high-temperature processes often occur at pressures  $\gg 1$  atm. In addition, melt compositions important to the understanding of volcanological processes always contain various amounts of volatile constituents, mainly H<sub>2</sub>O-, CO<sub>2</sub>-, and S-containing compounds.

Hence, there is a considerable mismatch between the available knowledge of melt viscosities (Bottinga and Weill, 1972; Shaw, 1972; Urbain et al., 1982; Dingwell and Webb, 1990; Kushiro, 1980; Ryan and Blevins, 1987) and that which is actually needed for understanding igneous processes. As is usual, the easy measurements have been done, and the more difficult ones remain to be done. Those more difficult measurements are (1) at temperatures between the glass transition and the liquidus temperature, where many melt compositions show an irre-

pressible tendency to crystallize, (2) at intermediate pressures on melts containing volatiles in solution, and (3) at high pressures on melts with and without dissolved volatiles. To fill these important gaps in our knowledge, one is tempted to extrapolate, but that is only possible if the phenomenon of silicate melt viscosity is understood quantitatively.

Liquid viscosity and the glass transition are two intimately related topics. Presently, research on the physics of these topics is quite active because it has become apparent that all types of liquids can be transformed into glasses under the right conditions. Moreover, transitions that very much resemble the glass transition but involve other physical properties have been discovered during the last two decades. Sethna et al. (1991) have published a concise survey of this field; other recent, very readable, accounts are by Scherer (1990) and Jäckle (1986). The study of the viscosity of liquids began early this century, and historical reviews are given in Brush (1962) and Sturm (1980). In this contribution we discuss liquid silicate viscosity and its temperature dependence, and we limit ourselves to considering only theories that are currently popular, namely, (1) the absolute rate theory of Eyring (Glasstone et al., 1941), (2) the free volume theory (Cohen and Grest, 1979), (3) the configurational entropy theory (Adam and Gibbs, 1965), and (4) the mode coupling theory (Götze, 1991). These theories will be examined in the light of the presently available data on silicate melts and the evident needs of Earth scientists for information on viscosities over extended ranges of temperature and composition.

### A SURVEY OF VISCOSITY THEORIES

The best-known equation for expressing the temperature dependence of the viscosity of silicate melts is the Arrhenius relation:

$$\eta(T) = A_a \exp(E_a/RT) \quad (1)$$

where  $A_a$  and  $E_a$  are adjustable constants,  $\eta$  is the viscosity,  $T$  the absolute temperature, and  $R$  the gas constant. Equation 1 is an approximation of a more complete equation derived from absolute rate theory by Eyring (Glasstone et al., 1941). The basic ingredient of absolute rate theory is the mechanism of hopping of individual atoms over a potential energy barrier of height  $E_a$ , the activation energy. Viscosity theories earlier derived by Frenkel (see Frenkel, 1955) and by Andrade (see Andrade, 1954) are also in agreement with Equation 1. Because this equation can be obtained in different ways, there is no unique attribution of a physical meaning to the adjustable constants.

The modern version of the free volume theory was developed by Cohen and Turnbull (1959) and later extended by Cohen and Grest (1979) and Grest and Cohen (1981). The basic assumption of this model is that atoms are confined to cells defined by their nearest neighbors. These cells can be liquid or solidlike, depending on whether their volume is larger or smaller than the critical volume ( $V_c$ ).  $V_c$  is assumed to be approximately equal to the atomic volume ( $V_m$ ). The excess volume with respect to  $V_c$  is called free volume ( $V_f$ ). Free exchange of free volume only takes place between liquidlike cells. The redistribution of free volume among the cells in a cluster of liquidlike cells can give rise to fluctuations in cellular volume. Atoms can diffuse when these fluctuations are greater than  $V_c$ . This reasoning permitted the evaluation of  $V_f$  and leads to the viscosity equation

$$\eta(T) = A_f \exp(2V_m z_0 / \{ (T - T_0) + [(T - T_0)^2 + 4V_a z_0 T]^{0.5} \}) \quad (2)$$

where  $A_f$ ,  $z_0$ ,  $T_0$ , and  $V_a$  are adjustable parameters to be obtained by fitting Equation 2 to viscosity data. This equation is a more sophisticated version of the well-known empirical Doolittle relation (1951)

$$\eta = A_0 \exp(-\gamma_0 V_m / V_f) \quad (3)$$

when one assumes that  $\gamma_0$  approximates unity and  $A_0 = A_f$ . The adjustable constants  $A_0$ ,  $V_b$ , and  $\gamma_0$  in Equation 3 are also evaluated by obtaining an optimal fit to measured viscosity values.

Adam and Gibbs (1965) generalized and extended earlier work (Gibbs and DiMarzio, 1958) on the configurational entropy theory to explain the relaxational properties of glass-forming liquids. According to their theory, the structural relaxation time of a liquid system is determined by the probabilities of configurational changes in microscopic volumes of liquid in the system. These changes are thought to be the outcome of cooperative rearrangements of the atomic constituents in these small

volumes of liquid. Adam and Gibbs (1965) obtained an expression for the ensemble average of these probabilities

$$\langle W(T) \rangle = A_w \exp[-B_c/(TS_{\text{conf}})] \quad (4)$$

where  $A_w$  and  $B_c$  are material-dependent parameters whose temperature dependencies are negligible in comparison with that of the product of  $T$  and the configurational entropy ( $S_{\text{conf}}$ ). The structural relaxation time ( $\tau$ ) is inversely proportional to the average probability of a structural rearrangement

$$\tau(T) = A_c \exp[B_c/(TS_{\text{conf}})] \quad (5)$$

and the viscosity is proportional to the structural relaxation time. In this paper the term structural relaxation time is used to indicate the shear strain relaxation time. The viscosity is given by

$$\eta(T) = A_e \exp[B_c/(TS_{\text{conf}})]. \quad (6)$$

$A_e$  and  $B_c$  are adjustable constants determined by fitting Equation 6 to viscosity observations.  $S_{\text{conf}}$  can be derived from calorimetric data; Richet and Bottinga (1986) and Richet and Neuville (1992) have reviewed such data for silicate liquids. The configurational entropy is a measure of the accessible number of configurational states ( $\Omega_{\text{conf}}$ )

$$S_{\text{conf}} = k \ln[\Omega_{\text{conf}}(T)] \quad (7)$$

where  $k$  is the Boltzmann constant. To a good approximation, silicate liquids have a Maxwellian rheologic behavior (Dingwell and Webb, 1990); hence

$$\eta = \tau G_\infty \quad (8)$$

where  $G_\infty$  is the shear modulus at infinite frequency. This modulus does not have a significant temperature dependence for silicate melts (as far as we know); it is about  $10^{10}$  Pa (Dingwell and Webb, 1989). The average value of  $A_e$  is about 0.003 Pa·s. This value was obtained by fitting Equation 6 to measured viscosities of liquid compositions for which the residual entropies at 0 K are known (Table 1). By means of Equations 5, 6, and 8, it follows that  $A_f$  has a value of about  $3 \times 10^{-13}$  s, i.e., a value compatible with the vibrational frequency of the silica network.

Mode coupling theory (MCT), like the free volume and configurational entropy theories, strives to explain the occurrence of the glass transition. An inevitable by-product of each of these theories is an expression for the viscosity as a function of temperature. The point of departure of mode coupling theory is that the number density of the atoms or molecules in the liquid increases when the temperature decreases and that, on approaching the glass transition, more and more particles are supposedly trapped for increasing time intervals in cages formed by their nearest neighbors. Because of this effect, the viscosity increases with decreasing temperature, and eventually the glass transition takes place when the translations of the particles are virtually frozen. The origin of MCT goes back to the work of Boltzmann at the end of the last century. This theory has drawn the attention of physicists

since Leutheuser (1984) and Bengtzelius et al. (1984) developed it to explain the glass transition. An extensive and explicit review of MCT has been published by Götze (1991).

In mode coupling theory, the change of the number density with falling temperature is determined by evaluating the evolution of the space-time correlation of normally occurring density fluctuations. These fluctuations affect particle positions and thus interparticle forces, which give rise to relaxation currents and retardation effects. As a result, density fluctuations are coupled nonlinearly. At a critical density, the particle motions become blocked and density currents cannot relax toward equilibrium; this causes the system to become nonergodic. MCT is still in a developmental stage (Schmitz et al., 1993) and cannot yet be applied to complicated liquids. The range of validity of the solutions obtained with this statistical treatment of a many-particle system is not known precisely. According to Götze (1991), the formulated equations describe the effects of cage formation, percolation, and back flow of particles in strongly interacting, densely packed systems. An important prediction of MCT is that, at temperatures in excess of a critical temperature ( $T_c$ ), the viscosity varies according to a power law

$$\eta(T) = \eta_0(T - T_c)^{-\gamma}. \quad (9)$$

The adjustable constants  $\eta_0$ ,  $T_c$ , and  $\gamma$  can be determined by fitting Equation 9 to measured viscosities.  $T_c$  is greater than  $T_g$ , the conventional glass transition temperature.

#### FLOW REGIMES IN SILICATE MELTS

In crystalline solids, various diffusion mechanisms can be operative, such as atoms hopping from one interstitial position to the next one, or jumping from defect to defect, etc. Which of these mechanisms is the most efficient depends usually on composition, pressure, and temperature. Mass transfer in liquids can also occur in different ways. Therefore it is highly unlikely that empirical relationships such as Equations 1 and 3 would be valid over extended viscosity ranges. In mode coupling theory, different flow regimes have been identified (Götze, 1991; Kim and Mazenko, 1992). Numerical simulations of flow in liquids by means of nonequilibrium molecular dynamics have also shown the existence of different mass transfer regimes (Heyes, 1986; Hoover, 1983).

Several authors have described a non-Newtonian flow behavior in silicate liquids (Li and Uhlmann, 1970; Simmons et al., 1982, 1988). This type of flow has also been recognized in natural silicate liquids (Webb and Dingwell, 1990a). But even with the restriction of Newtonian flow, at least three flow regimes may be distinguished: (1)  $\eta > 10^{12}$  Pa·s,  $T < T_g$ , where the liquid has transformed into glass; (2)  $1 < \eta < 10^{12}$  Pa·s, where for the great majority of silicate liquids the observed viscosity and its temperature dependence is best described by Equation 6; and (3)  $\eta < 1$  Pa·s, where liquid silicates conform to Equation 9. The indicated viscosities limiting the three flow regimes should not be taken as precisely determined

**TABLE 1.** Residual entropy at 0 K and heat capacities at  $T_g$  (J/gfw·K)

Substance	$T_g$ (K)	$S_{res}(0)$	$C_{p, glass}$	$3nR$	$C_{p, liq}$	Ref.
SiO <sub>2</sub>	1480	5.1	73.4	74.8	81.4	1
MgSiO <sub>3</sub>	1056	11.2	124.9	124.7	167.2	2
Mg <sub>2</sub> SiO <sub>4</sub>	990	0.8	n.d.	174.6	252.9	3
CaSiO <sub>3</sub>	1065	8.8	131.8	124.7	167.4	4
CaMgSi <sub>2</sub> O <sub>6</sub>	1005	23.0	256.3	249.4	334.6	5
Mg <sub>3</sub> Al <sub>2</sub> Si <sub>5</sub> O <sub>12</sub>	1020	56.3	515.8	498.9	679.2	6
NaAlSi <sub>3</sub> O <sub>8</sub>	1033	9.7	173.5	174.6	203.4	7
NaAlSi <sub>2</sub> O <sub>6</sub>	1130	16.0	252.2	249.4	278.2	8
NaAlSi <sub>3</sub> O <sub>8</sub>	1096	36.7	320.7	324.3	347.4	1
KAlSi <sub>3</sub> O <sub>8</sub>	1200	28.3	316.0	324.3	337.5	1
CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	1160	36.8	329.4	324.6	424.2	1

Note: n.d. = not determined. Reference abbreviations are as follows: 1 = Richet (1984); 2 = Courtial and Richet (1993); 3 = Richet et al. (1993a); 4 = Richet et al. (1991); 5 = Richet et al. (1986); 6 = Téquie et al. (1991); 7 = Richet and Neuville (1992); and 8 = Richet et al. (1993b).

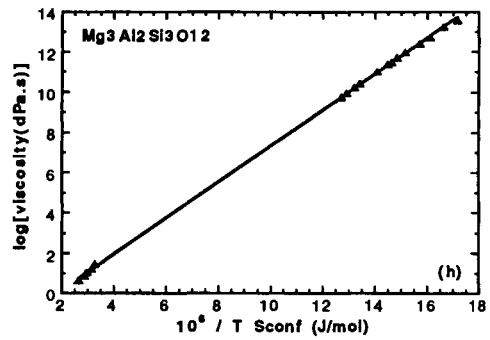
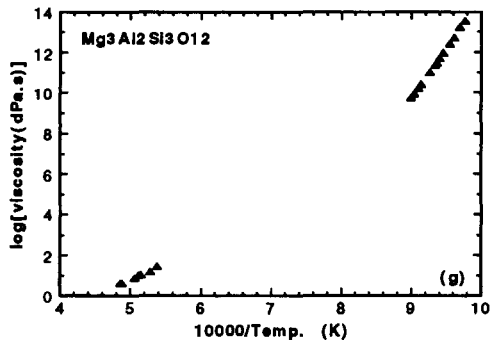
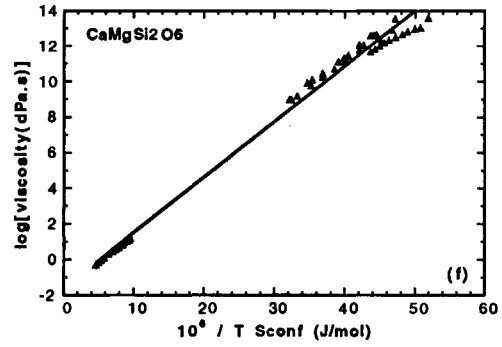
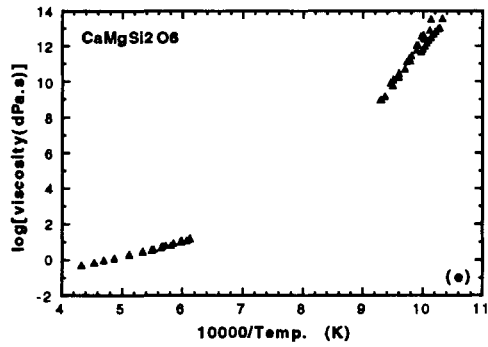
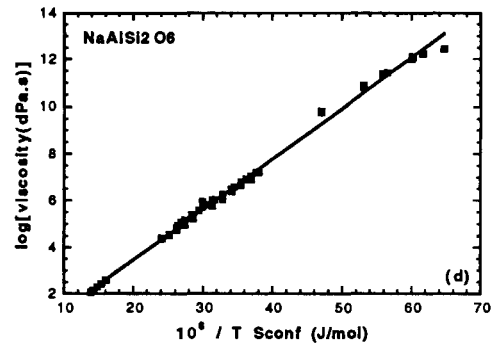
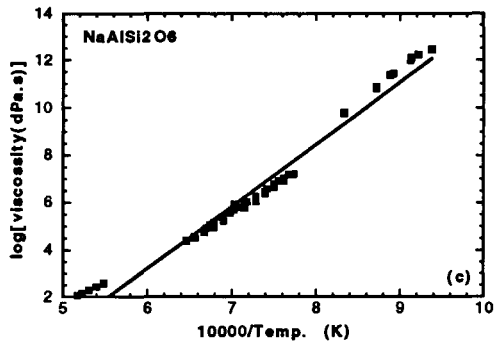
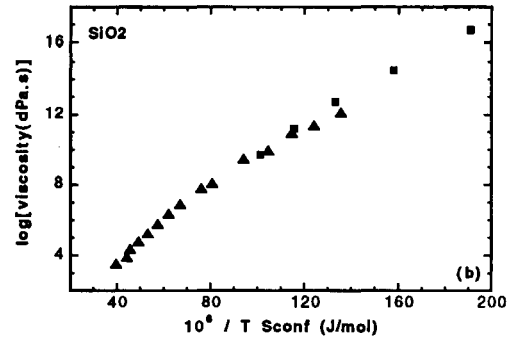
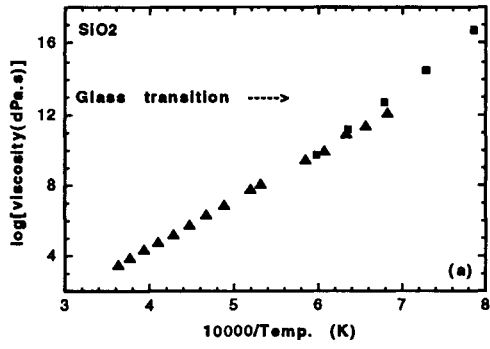
values. Their approximate nature is discussed in the next sections, where these regimes are described in greater detail.

#### Intermediate viscosity regime

The intermediate regime is dealt with first, because most silicate melt viscosities have been measured in the interval  $1 < \eta < 10^{12}$  Pa·s. Virtually all igneous and volcanic processes involving silicate liquids (i.e., lava transfer, crystal and bubble growth, crystal and bubble movement with respect to the liquid, and magma mixing) take place in this viscosity interval. Figure 1e and 1g illustrates the well-known fact that melts not fully polymerized show very important increases in their activation energy of viscous flow in the viscosity interval under discussion. Such changes have as a result that, in the vicinity of  $T_g$ , the viscosity of liquid anorthite increases by an order of magnitude for a decrease in temperature of  $< 25$  °C (Hummel and Arndt, 1985). Similar increases have been observed for other melt compositions, e.g., pyrope (Neuville and Richet, 1991) and diopside (Kirkpatrick, 1974). In geophysical models of petrological processes or magma transfer, this feature tends to be ignored; usually, one assumes that the melt has a characteristic viscosity, which is temperature independent. Obviously, realistic modeling is not possible without the use of the correct equation for the rheology of silicate melts.

Numerous empirical, semiempirical, and theoretical viscosity equations have been proposed since the beginning of this century, and 17 of them have been tested by Sturm (1980). In our experience, Equation 6 (Adam and Gibbs, 1965) reproduces measurements on silicate melts in this viscosity range better than any other equation. The allegation that Equation 6 "overestimates the temperature dependence of the viscosity in the vicinity of  $T_g$ " (Scherer, 1990) has not been verified for liquid silicates.

The free volume and the Adam-Gibbs (A-G) theories are, to a large extent, mutually compatible. Free volume and configurational entropy are physically related and temperature dependent. This is the reason that models using these concepts predict that the partial derivative of



the logarithm of viscosity with respect to reciprocal temperature increases with decreasing temperature. This latter feature distinguishes these models from those obeying the Arrhenius equation. However, the free volume is not a directly observable quantity and cannot be evaluated quantitatively. On the contrary, the configurational entropy of liquid silicates can be determined without great difficulty. The Arrhenius equation (Eq. 3), with a temperature-independent activation energy, cannot be a generally valid expression of the temperature dependence of intermediate viscosities because of the universal occurrence of the glass transition.

Equation 6 is remarkable because it contains only two adjustable parameters; of course, if the configurational entropy of the melt is not known, it becomes nonunique in this respect. In Table 1 we list the melt compositions for which the thermodynamic constants needed for the calculation of  $S_{\text{conf}}$  have been measured. Figure 1 shows the quality of the fits of Equations 6 and 1 to the viscosity data for some of these melts. Figure 2 is a plot of the calorimetrically determined configurational entropy vs. the same quantity obtained by fitting Equation 6 to viscosity measurements, where, in addition to  $A_e$  and  $B_e$ ,  $S_{\text{conf}}$  at  $T = T_g$  has been considered as an adjustable parameter (Richet, 1984). The very good agreement between these two independently derived configurational entropies (Fig. 2) is the experimental justification for Equation 6. The simple shape of the curves (Fig. 1), which is typical for nearly all silicate melts, is the reason that no more than three adjustable constants are needed. Fitting equations with more adjustable constants to viscosity data often results in poorly defined values, which may be devoid of physical sense. Hence viscosity data provide insufficient information for the determination of the four adjustable constants for Equation 2 proposed by Cohen and Grest (1979).

Scherer (1992), Angell and Sichina (1976), and other authors have remarked that the well-known empirical VTF (Vogel, 1921; Tammann and Hesse, 1926; Fulcher, 1925) equation

$$\eta(T) = A_{\text{VTF}} \exp[B_{\text{VTF}}/(T - T_0)] \quad (10)$$

is a good mathematical approximation to Equation 6, provided that the specific heat difference  $C_{\text{P,liq}} - C_{\text{P,glass}}$  is proportional to  $1/T$ . In Equation 10,  $A_{\text{VTF}}$ ,  $B_{\text{VTF}}$ , and  $T_0$  are adjustable constants. The isobaric specific-heat measurements on silicate liquids and the corresponding glasses made in our laboratory indicate unambiguously that this postulated proportionality is not valid for silicates

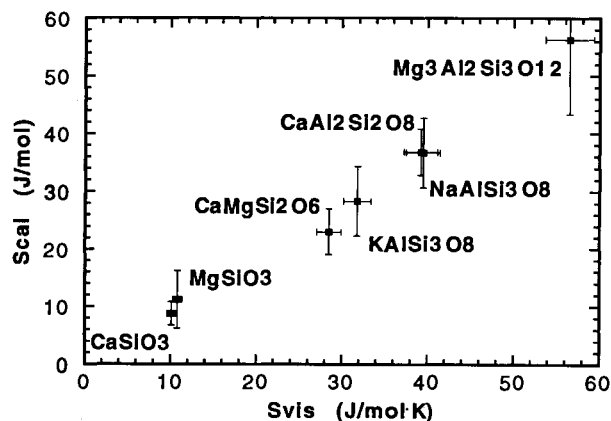


Fig. 2. Calorimetrically determined residual entropy at 0 K ( $S_{\text{cal}}$ ) plotted vs. configurational entropy at  $T_g$  ( $S_{\text{vis}}$ ) obtained from the best fit of Eq. 6 to viscosity observations, with the terms  $A_e$ ,  $B_e$ , and  $S_{\text{conf}}$  treated as adjustable parameters.

(Richet et al., 1984; Richet and Bottinga, 1986). Nevertheless, Equation 10 reproduces quite well the temperature dependence of the viscosity of silicate liquids.

To derive Equation 4, Adam and Gibbs (1965) postulated that when a liquid system approaches the glass transition, it contains subsystems that can rearrange individually into other configurations independently of their immediate environment. Such rearrangements are triggered by normal thermodynamic fluctuations. Using standard statistical mechanics, they obtained an expression for the ensemble average of the transition probability of the system:

$$\langle W(T) \rangle = A_w \exp[-z^* \Delta\mu/(kT)]. \quad (11)$$

In this equation,  $z^*$  is the minimum number of particles a rearranging subsystem must have before it can undergo a transition to another configurational state. The chemical potentials of the particles in a subsystem capable of a transition and those in a subsystem unable to change its configuration differ by an amount  $\Delta\mu$ . Equation 11 is the basis of the A-G model. The number  $z^*$  depends on temperature and becomes larger as  $T$  decreases, which causes a diminution of the transition probability (Eq. 11).

The merits of the Adam-Gibbs theory have been described previously; qualitative aspects were discussed by Chang et al. (1966) and Angell and Sichina (1976), relaxation processes by Scherer (1984), and the temperature dependence of silicate melt viscosities by Richet (1984) and Richet and Neuville (1992). Since then, new devel-

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Fig. 1. Logarithm of viscosity (dPa·s) vs. reciprocal temperature for a–h. (a)  $\text{SiO}_2$ ; data from Urbain et al. (1982) and Hetherington et al. (1964). The data of Hetherington et al. were preferred to those of Fontana and Plummer (1966) because they were in better agreement with the relaxation times at 1100 °C determined by Krol et al. (1986). (b) Same data plotted vs.  $1/TS_{\text{conf}}$ . (c)  $\text{NaAlSi}_3\text{O}_8$ ; data from Riebling (1966), Stein and Spera (1993), and Taylor and Rindone (1970). (d) Same data as plotted in c. (e)  $\text{CaMgSi}_2\text{O}_6$ ; data from Neuville and Richet (1991), Tauber and Arndt (1986), Scarfe et al. (1983), and Urbain et al. (1982). (f) Same data as plotted in e. (g)  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  data from Neuville and Richet (1991). (h) Same data as plotted in g.

opments have taken place that provide additional independent support for this theory. The A-G theory was used to elucidate the development of nanometric heterogeneities observed in liquids close to the glass transition (Moynihan and Schroeder, 1993). It was also used to interpret the occurrence of viscous thinning in silicate liquids (Bottinga, 1994a, 1994b).

When the A-G theory was developed, the change from Newtonian to non-Newtonian rheology in silicate liquids as the stress is increased beyond a certain level was not well known. Since then, this phenomenon has been observed repeatedly in these liquids; well-documented descriptions have been published by Li and Uhlmann (1970), Simmons et al. (1982, 1988), Dingwell and Webb (1989), and Webb and Dingwell (1990a, 1990b). The A-G theory is basically an equilibrium theory. During viscosity measurements the liquid system is required to flow, but the applied stress is small enough that the equilibrium properties of the system are not perturbed to a measurable extent. For this reason, one can use in Equation 6 the configurational entropy measured on the system in a state of internal equilibrium, as has been shown by Richet (1984). According to Bottinga (1994a, 1994b) viscous thinning is the consequence of the production of configurational entropy due to the work done by an applied stress on the system. Under conditions of moderate stress, i.e., less than approximately  $10^8$  Pa, this contribution to  $S_{\text{conf}}$  is negligible when compared with the equilibrium value of  $S_{\text{conf}}$ , but at greater stress it should not be ignored. Hence beyond a certain level of stress, the viscosity becomes measurably stress dependent, i.e., non-Newtonian, as reported in the papers cited above. This analysis of non-Newtonian viscosity shows that if one deals with a system not in an equilibrium state, i.e., a system whose fictive temperature is significantly different from the externally imposed temperature, the application of Equation 6 requires an evaluation of  $S_{\text{conf}}$ , which takes into account the effect of this disequilibrium.

Moynihan and Schroeder (1993) have shown that spectroscopically inferred, nanometric density heterogeneities in liquids close to the glass transition can be interpreted as configurational entropy fluctuations. This interpretation is conformable to one of the provisions of Adam and Gibbs (1965). The ensemble average  $\langle \Delta S \Delta V \rangle$  is given by (Landau and Lifshitz, 1958)

$$\langle \Delta S \Delta V \rangle = kT(\partial V / \partial T)_P \quad (12)$$

where  $\Delta S$  and  $\Delta V$  are the amplitudes of entropy and volume fluctuations. By means of Equation 12, one derives (Robertson, 1978)

$$\langle \Delta S_{\text{conf}} \Delta V \rangle = kT[(\partial V_{\text{liq}} / \partial T)_P - (\partial V_{\text{glass}} / \partial T)_P]. \quad (13)$$

Hence the fluctuations  $\Delta S_{\text{conf}}$  and  $\Delta V$  are correlated. Therefore, the presence of density heterogeneities implies the presence of configurational entropy heterogeneities as well. Moynihan and Schroeder (1993) have pointed out that the introduction of these configurational entropy fluctuations into Equation 5 explains the observed nonex-

ponential structural relaxation kinetics in liquids in the vicinity of  $T_g$ . Detailed descriptions of the relaxation kinetics close to the glass transition can be found for  $B_2O_3$  in Macedo and Litovitz (1965), for  $GeO_2$  in Napolitano and Macedo (1968), and for silicates in Webb (1991) and Bagdassarov et al. (1993).

The occurrence of entropy fluctuations just above  $T_g$  is consistent with the well-known specific heat change associated with the glass transition. Adam and Gibbs (1965) and Richet (1984) interpreted this phenomenon in terms of  $\Delta C_P$ , the difference between the liquid and glass heat capacities at constant pressure. The specific heat is related to entropy fluctuations (Landau and Lifshitz, 1958) by

$$\langle (\Delta S)^2 \rangle = kC_P \quad (14)$$

and this gives (Robertson, 1978)

$$\langle (\Delta S_{\text{conf}})^2 \rangle = k(C_{P,\text{liq}} - C_{P,\text{glass}}) = k\Delta C_P. \quad (15)$$

As a liquid is cooled from above  $T_g$ , it adjusts its internal structure without delay. This adjustment is possible because of the occurrence of normal thermodynamic fluctuations whose magnitudes decrease with falling temperature within the body of the liquid. At  $T < T_g$  the rate of structural adaptation in the liquid slows down considerably, and the liquid transforms into a glass. The internal structure of the glass has been inherited from the liquid at the temperature at which the glass transition takes place. This temperature depends on the rate of cooling. But once the glass transition has been passed, the structure of the glass does not change much with  $T$  except for the effects of thermal expansion or contraction. All liquids can be transformed into a glass under the appropriate conditions; the occurrence of a glass transition is not restricted to the so-called glass-forming liquids.

Moynihan and Schroeder (1993) have interpreted the heretofore mentioned heterogeneities to be expressions of the postulated A-G subsystems. These heterogeneities have been observed spectroscopically by several groups of authors (Malinovsky and Sokolov, 1986; Sokolov et al., 1993; Duval et al., 1990) and have also been discussed by Mazurin and Porai-Koshits (1989). Close to  $T_g$ , these heterogeneities become observable because of their size, i.e., large  $z^*$ , and the concomitant large value of  $\tau$  (Eqs. 11, 4, and 5). The size of these heterogeneities has been reported to range from 2 to 5 nm. Moynihan and Schroeder (1993) have calculated a volume of about  $12 \text{ nm}^3$  for heterogeneities observed in liquid  $B_2O_3$ , which would contain about 400 formula units. In view of these numbers, it is not surprising that Steinhardt et al. (1983), Dasgupta et al. (1991), Ernst et al. (1991), and others were unable to determine a correlation length or bond orientational order associated with the glass transition by conducting molecular dynamics studies with  $< 600$  particles.

Glasses, and in particular silica glass, have anomalous thermal and mechanical properties at very low temperature (see Krause and Kurkjian, 1968). In the present context, the observed excess specific heat (Pohl, 1981), with respect to the Debye value, and the anomalous vibra-

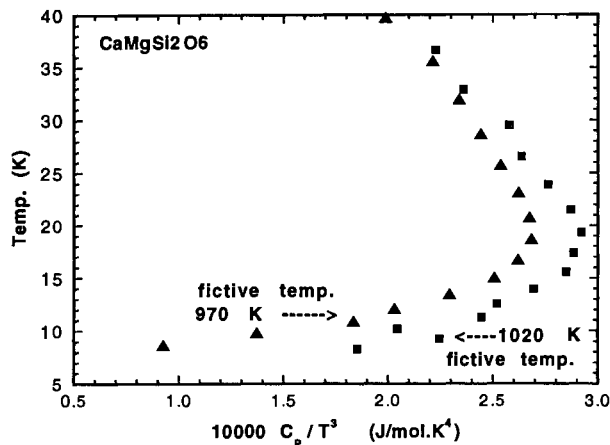


Fig. 3. Low-temperature isobaric molar heat capacity of  $\text{CaMgSi}_2\text{O}_6$ ; the fictive temperatures indicate the temperatures at which the two samples passed the glass transition during their quench from the liquid state. According to the Debye theory,  $C_p/T^3$  should be independent of  $T$  in the vicinity of 0 K.

tional properties at  $2 < T \text{ (K)} < 20$  are of great interest. Low-temperature vibrational properties of silica glass have been observed by Buchenau et al. (1984) by means of neutron scattering and were interpreted to be due to acoustic phonons and low-frequency modes associated with coupled rotations of  $\text{SiO}_4$  tetrahedra. These authors have shown that the specific heat of silica calculated from their neutron scattering data is in qualitative agreement with the specific heat anomaly around 15 K. These results support the Moynihan and Schroeder (1993) suggestion that heterogeneities observed in melts close to  $T_g$  may also contribute to the anomalous  $C_p$  of glasses at low temperature; or, more explicitly, the low- $T$  specific heat anomalies could be caused by density fluctuations frozen in at  $T = T_g$ . The observation that the specific heat anomaly of silica glass around 2 K is affected by the fictive temperature (Fagaly and Bohn, 1981) supports this interpretation. Richet et al. (1986) have also observed a fictive temperature dependence of the low-temperature  $C_p$  anomaly of vitreous diopside (Fig. 3). No satisfactory explanations for these specific heat anomalies and their fictive temperature dependence have yet been published.

The glass transition in simple liquids has been intensively studied by molecular dynamics (MD), in particular for liquid Ar. Figure 4 illustrates our results of a numerical calculation of the energy of liquid Ar at  $P = 9.5$  kbar and  $T = 140$  K. These results were obtained by means of a Monte Carlo simulation of an ensemble of 432 particles at constant pressure and temperature, with the same conventional interatomic potential as used by Yonezawa (1991). Initially the system is liquid with a high energy. As it seeks the equilibrium state in phase space, the energy decreases and reaches a plateau, and finally the system finds the stable state characterized by an energy minimum. This state is reached when the system crystallizes; the intermediate plateau, where the system is metastable,

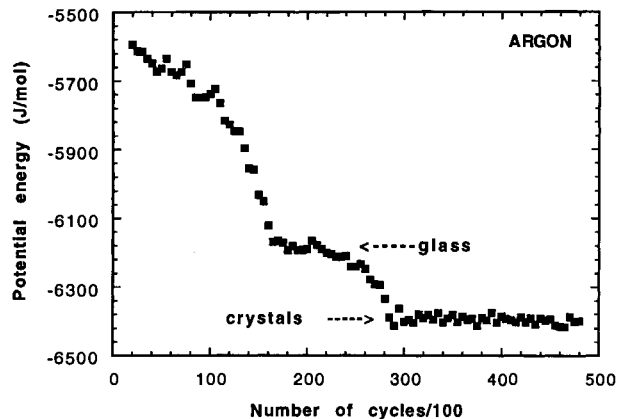


Fig. 4. Potential energy of Lennard-Jones particles (Ar) at 140 K and 9.5 kbar during a Monte Carlo simulation at constant  $T$  and  $P$  of a system of 432 particles.

represents the vitreous state. Yonezawa (1991) has published the results of a beautiful MD simulation showing the structure of liquid Ar in the neighborhood of  $T_g$ . She observed in her numerical experiments that, close to  $T_g$ , clusters of  $^{19}\text{Ar}$  atoms were formed, each atom enclosed in a Voronoi icosahedron. According to Frank (1952), such an arrangement corresponds to a minimum of the potential energy in a disordered system.

This picture of the glass transition in liquid Ar is rather simple, but it becomes more complicated in silicate liquids because of the accompanying occurrence of polymerization. A recent report on how changes in polymerization affect the glass transition temperature of silicate melts was published by Dingwell and Webb (1992), who made use of the fluxing effect of F and measured how the addition of F to a molten silicate lowered its glass transition temperature. However, it is well established that polymerization and glass formation are different phenomena. Polymerization affects glass formation, as shown by the observations of Dingwell and Webb (1992), but it is not a prerequisite. Many liquids do not polymerize at all, but under the right conditions they form glasses; examples are Ar and  $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$  (Grimsditch and Torell, 1989). The great majority of silicate liquids are only partially polymerized when the glass transformation intervenes. Liquid forsterite is very difficult to undercool and to transform into a glass (Richet et al., 1993a); it is one of the rare nonpolymerized silicate liquids, free of fluxing agents like  $\text{H}_2\text{O}$ , F, etc., at subliquidus temperatures. The opposite extreme is liquid silica at the cristobalite melting point, which is probably the most extensively polymerized silicate liquid. In the absence of fluxing agents, liquid forsterite and silica are, respectively, the most fluid and most viscous silicate melts at the melting temperatures of their isochemical crystalline phases.

It is not evident a priori that the constant  $B_c$  in Equation 6 remains unchanged while the polymerization reaction in the melt advances. However, the curves shown

in Figure 1 were calculated assuming the dependence of  $B_c$  on this process to be negligible in comparison with the variation of the product  $TS_{\text{conf}}$ . On the other hand, the degree of polymerization of the melts listed in Table 1 may have remained constant while the temperature changed and the viscosity increased to  $10^{12}$  Pa·s. In any case, Equation 6 has been shown to be valid for the intermediate viscosity regime. If there were polymerization effects, they would have been taken care of by means of the observed changes in  $S_{\text{conf}}$  with temperature.

### High-viscosity regime

The high viscosities considered in this section are characteristic of unaltered glassy rocks. Under stress, they fracture, i.e., they behave as elastic solids. But their behavior can be viscous under conditions of very slowly changing stress applied for long periods at temperatures somewhat less than  $T_g$ . Intrusive, highly polymerized silicate liquids, which do not easily crystallize, may show this mode of deformation in regions under tectonic stress.

Haggerty et al. (1968) noticed that the heat capacity of inorganic glasses close to  $T_g$  attains a value of  $3R$  per g·atom·K, i.e., the well-known molar heat capacity of harmonic oscillators. These authors interpreted this to mean that all the vibrational modes of the glass were excited when the glass transition was approached from below. This observation has been confirmed for silicate melts (Richet and Bottinga, 1986; Richet and Neuville, 1992). It implies that specific heat measurements give no indication of important configurational contributions to  $C_{p,\text{glass}}$  and to the entropy in the interval  $0 < T < T_g$ ; it justifies the Adam and Gibbs (1965) approximations that  $C_{p,\text{conf}} = 0$  when  $T < T_g$  and that the configurational entropy at the glass transition is given by the residual entropy at 0 K.

At  $T = T_g$  the specific heat of silicate melts decreases suddenly with falling temperature, or the derivative  $\partial C_p / \partial T$  diminishes anomalously (Richet, 1984), and the partial derivative of the logarithm of the spin lattice relaxation time for  $^{29}\text{Si}$  with respect to reciprocal temperature grows significantly (Liu et al., 1987, 1988; Farnan and Stebbins, 1990). Anomalies have been observed also for the coefficient of thermal expansion (Napolitano and Macedo, 1968; Knoche et al., 1992a, 1992b) and the compressibility (Krol et al., 1986). Another nice example of a consequence of the glass transition is the onset of an increase of the mean square displacement of Se atoms in vitreous Se for frequencies above  $10^{11}$  Hz at  $T > T_g$  (Buchenau and Zorn, 1992). All these changes are compatible with an important increase in the structural relaxation time and thus with a diminution of the number of available configurational states of the system when temperature drops below  $T_g$ .

The calorimetrically determined glass transition temperature ( $T_{g,\text{enth}}$ ) is usually higher than the temperature ( $T_{g,\text{vis}}$ ) at which the melt viscosity attains the value of  $10^{12}$  Pa·s (Neuville and Richet, 1991). The difference  $T_{g,\text{enth}} - T_{g,\text{vis}}$  is related to the different time intervals ( $\tau_{\text{probe}}$ ) the silicate liquid is probed during calorimetric and viscosity

measurements (see Richet and Bottinga, 1984a, 1984b). The techniques employed for the observation of different physical properties have different  $\tau_{\text{probe}}$  values and thus indicate somewhat different values of  $T_g$ . Moreover, it may happen that the relaxation times for enthalpy disturbances is not the same as for shear stress, this is also a reason for  $T_{g,\text{enth}}$  not to equal  $T_{g,\text{vis}}$  (see Angell, 1991; Grimsditch and Torell, 1989). However, for liquid silicates this latter effect has not been observed yet.

The amount of configurational entropy frozen in with  $T$  decreasing through the glass transition can be evaluated by measuring the residual entropy of the glass at 0 K, when the vibrational entropy is zero (Richet et al., 1986; Richet and Neuville, 1992). Table 1 is a list of the silicate glass compositions for which residual entropies have been measured. Residual entropy determinations are only possible for glasses obtained from silicate melts for which the equilibrium crystallization temperature and the heat of crystallization are known because they require the determination of absolute entropies. This implies the use of a standard state whose entropy is known, for example the perfect crystal at 0 K, whose entropy is zero. The residual entropy represents configurational states frozen in the system, i.e., states to which the system no longer has access. The loss of access to configurational states is not abrupt, but, because of the exponential character of Equation 5, the relaxation time suddenly becomes large on the time scale of human experience. Calorimetrically the gradual loss of configurational states at  $T < T_g$  cannot be observed because the time interval that the liquid is probed during a calorimetric measurement is smaller than  $\tau$  at low temperatures.

Evidently, the glass transition is not marked by a universal value of frozen-in configurational entropy (see Table 1). The transition expresses the fact that the structural relaxation time has reached a value corresponding to a viscosity of  $10^{12}$  Pa·s. Using Equation 8, one obtains  $\tau$  equal to 100 s if  $G_\infty = 10^{10}$  Pa at  $T = T_g$ . Stable viscosities in excess of  $10^{15}$  Pa·s can be measured by observing at subsequent times and at constant temperature the slowly converging changes of viscosities of compositionally identical glass samples with initially different fictive temperatures. The viscosities change because of slow adjustment of the internal structures of the samples to the imposed experimental temperature (Fig. 5). Such measurements demonstrate that not all the configurational states of a liquid are frozen in just below  $T_g$ . Hence at  $T < T_g$ ,  $S_{\text{conf}} > 0$ , but its variation with  $T$  cannot be measured because there is no way directly to measure  $C_{p,\text{conf}}$  at  $T < T_g$  (see Johari and Goldstein, 1970).

The A-G mechanism of deformation is likely to become ineffective at  $T < T_g$ , when only large A-G subsystems can still have access to some alternative configurational states by cooperative rearrangements of their constituent particles. In other words, at  $T < T_g$ , only microscopic volumes with large  $z^*$  have significant values for their transition probability (Eq. 11). Under such conditions the apparent activation energy of the viscosity is



quite large. If indeed at low temperature the A-G mechanism becomes ineffective, then another flow mechanism should replace it because, even at low temperatures, glasses can be deformed. This as-of-yet new and unidentified mechanism should have an activation energy smaller than that of the A-G mechanism.

Available evidence, in particular the high-viscosity measurements by Li and Uhlmann (1970) on  $0.08\text{Rb}_2\text{O}\cdot 0.92\text{SiO}_2$ , suggests that the viscosity is Arrhenian at  $T < T_g$ , according to Angell (1991). But a demonstration that the viscosity becomes Arrhenian at  $T < T_g$  is not a proof of the operation of a different flow mechanism. At these temperatures the viscosity increases rapidly with decreasing  $T$ : a drop of  $<25$  K may cause an increase of the viscosity by more than one order of magnitude. The variation of the viscosity with falling  $T$  for a variety of compositions can be larger than what has been observed for silica by Hetherington et al. (1964). Hence measurements at  $T < T_g$  are over small temperature intervals where  $S_{\text{conf}}$  is virtually constant. Therefore, the variation of the logarithm of viscosity with reciprocal temperature is linear or very close to it and in agreement with Equation 6 as well as Equation 1.

A few series of measurements done in our laboratory and elsewhere show that the difference between the activation energies for viscous flow at  $T > T_g$  and at  $T < T_g$  can be positive or negative (Fig. 6). The absolute values of the differences are significant, about 25% of the values of the activation energy at temperatures close to  $T_g$ . One should be aware that viscosity measurements at  $T < T_g$  always require long annealing times to ensure that the fictive temperature of the glass sample is equal to the real temperature. If annealing is not properly done, the sample will not be correctly stabilized, which causes the observed viscosity to be too low. The observations by Hetherington et al. (1964) on silica are a very nice illustration of these effects. If the glass was correctly stabilized, viscosity measurements done at decreasing temperatures, from  $T > T_g$  to  $T < T_g$ , may show (1) a continuous increase of the (apparent) activation energy ( $E$ ) (see Fig. 6a), which means that the A-G mechanism is operative and  $C_{p,\text{conf}}$  diminishes continuously; (2) no change of  $E$  when  $T = T_g$ , but the activation energy at  $T > T_g$  is smaller than that at  $T < T_g$  (see Figs. 1a and 6b), which indicates that at  $T < T_g$ ,  $S_{\text{conf}}$  is constant and the A-G mechanism is still active; and (3)  $E$  is constant at  $T < T_g$  and is smaller than at  $T > T_g$  (see Fig. 6c). Here the A-G structural relaxation time has become longer than that of another competing relaxation mechanism, and the viscosity is now truly Arrhenian.

To show the change of slope in the variation of the logarithm of viscosity with reciprocal temperature occurring at  $T = T_g$ , we have fitted different Arrhenius equations to viscosity data, larger and smaller than  $10^{12}$  Pa·s, for 15 silicate compositions (see, for example, Fig. 6a and 6c) and calculated the changes in activation energy associated with the passage of this conventional glass transition value. Our results do not show convincingly that

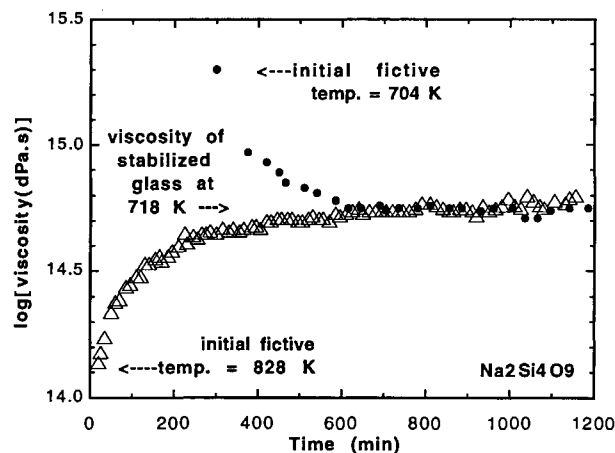


Fig. 5. Viscosity of  $\text{Na}_2\text{Si}_4\text{O}_9$  at 718 K (Sipp, 1993).

at  $T = T_g$  the flow mechanism changes from A-G to that of Eyring (Glasstone et al., 1941), Andrade (1954), or Frenkel (1955). Most of the results conform to case 1 above. The best-known example of case 3 is  $\text{GeO}_2$  (see Fig. 6c). None of the silicate viscosity data measured at  $T < T_g$  varies with temperature in such a way that the activation energy becomes  $<250$  kJ/mol, as has been reported (Yinnon and Cooper, 1980; Schaeffer, 1975) for the low-temperature self-diffusion of O in silicate glasses. Nevertheless, it seems reasonable to conclude that somewhere at  $T < T_g$  the A-G flow mechanism becomes inadequate to dissipate accumulating elastic shear strains when the glass is under stress. Therefore, it is replaced by another mechanism to take care of the required relaxation. The example of  $\text{GeO}_2$  may show this change (Fig. 6c).

#### Low-viscosity regime

The low-viscosity regime is of interest to Earth scientists because depolymerized silicate melts rich in network modifiers, such as  $\text{H}_2\text{O}$ , F, Ti, etc., have very small viscosities, and their extrapolation to high temperatures and pressures requires an understanding of the rheology of these melts. These silicate liquids are often assumed to be involved in processes like metasomatism and to be present in the upper mantle (Naumov and Kovalenko, 1986; Thompson, 1992; Hauri et al., 1993; Schrauder and Navon, 1994). Mafic melts in the upper mantle should be depolymerized because of high pressure; these liquids could have viscosities low enough to belong to the category discussed in the following paragraphs.

Application of Equation 6 when  $T > T_g$  requires the evaluation of  $S_{\text{conf}}$ . This can be done using standard thermodynamics and the known values of  $S_{\text{conf}}$  at  $T = T_g$ , together with the configurational heat capacity. For silicate liquids the configurational entropy at  $T_g$  is equal to the residual entropy at 0 K, which can be measured by low-temperature adiabatic calorimetry, and  $C_{p,\text{conf}}$  can be calculated using the approximation

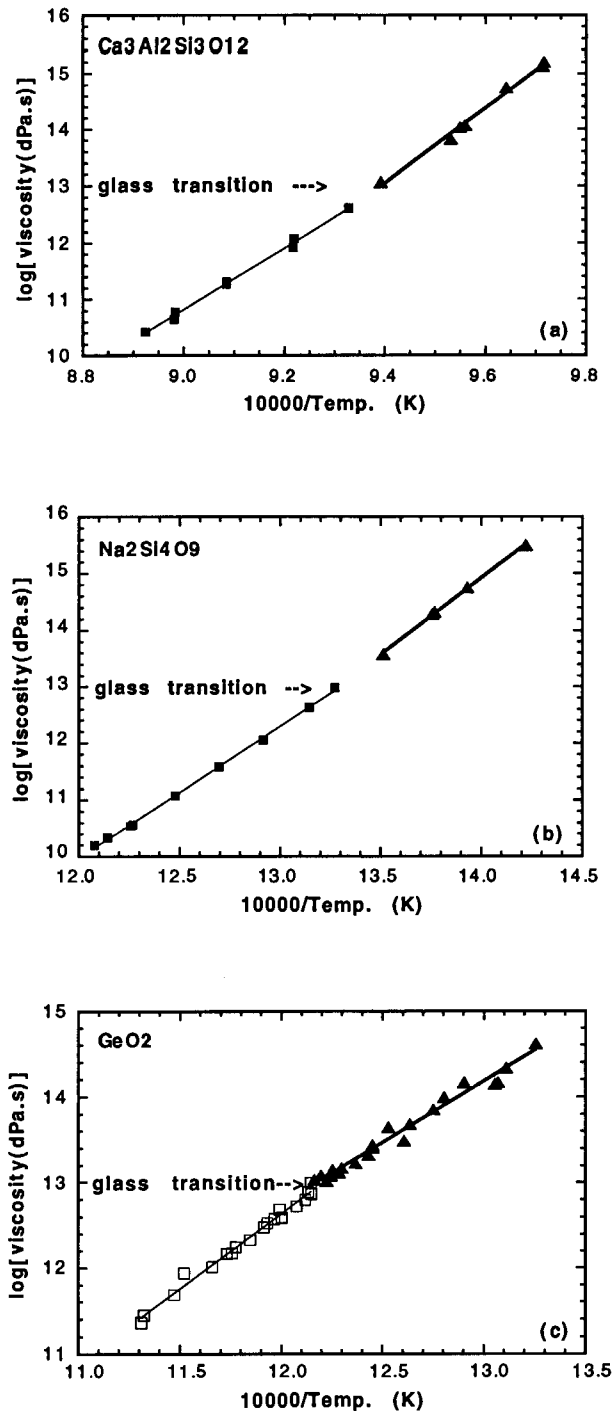


Fig. 6. Logarithm of viscosity vs. reciprocal temperature. (a)  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  (grossular) data from Sipp (1993). The activation energy at  $T < T_g$  is larger than for  $T > T_g$ . The measurements were done with the apparatus described in Neuville and Richet (1991). (b)  $\text{Na}_2\text{Si}_4\text{O}_9$  (Sipp, 1993; Neuville and Richet, 1991). Data below and above  $T_g$  are in perfect continuity; at  $T < T_g$  the data appear to be Arrhenian, but the activation energy is larger than at high  $T$ . Perhaps the largest viscosity value is too small because the glass may have been incompletely stabilized. (c)  $\text{GeO}_2$ ; data from Fontana and Plummer (1966) and Napolitano and Macedo (1968). At  $T < T_g$  the viscosity is Arrhenian, with an activation energy smaller than for  $T > T_g$ .

tional and vibrational entropies become less distinct, and vibrational degrees of freedom become increasingly anharmonic and may acquire rotational characteristics.

At  $T \gg T_g$ , the minimum size of an A-G subsystem able to have access to an alternative configurational state by means of a cooperative rearrangement of its particles becomes so small that the notion of a subsystem is meaningless. Hence there should be a high-temperature limit to the applicability of the A-G theory.  $S_{\text{conf}}$  grows with  $T$ ; therefore at high temperature the availability of configurational states becomes large enough eventually that it does not restrict any longer the fluidity of the melt. Consequently, the liquid viscosity becomes independent of  $S_{\text{conf}}$ , and another mechanism limits the strain rate of the stressed liquid at  $T \gg T_g$ .

When the viscosity becomes smaller than 1 Pa·s, a rheological change occurs, according to Taborek et al. (1986), who reported data for about 20 different liquids. At  $T/T_g > 1.25$ , the viscosities of these liquids varied with temperature in accordance with Equation 9; most of the time the value of  $\gamma$  was close to 2, as predicted by the mode coupling theory (Götze, 1991). There are very few published measurements on silicate liquids with  $\eta < 1$  Pa·s and a precision better than 10%. Hence a satisfactory verification of the validity of Equation 9 for these low-viscosity liquids is not possible at this moment. Figure 7 shows examples illustrating the superiority of Equation 9 over the Arrhenius equation.

## RECOMMENDATIONS

Before 1970, the word viscosity was hardly mentioned in petrology textbooks. Fortunately, this is no longer the case. But very frequently it is assumed a priori that liquid silicate viscosities vary with temperature in Arrhenian fashion. Indeed the syntheses of available information published by Bottinga and Weill (1972) and Shaw (1972) gave the impression that this was the case. There are at least two reasons for this impression. The first and most important is that only high-temperature data were considered by Bottinga and Weill (1972) and Shaw (1972). The other reason is that the temperature dependence could be determined only approximately because of the wide error margins of the observations. On the other hand, Urbain et al. (1982) reported non-Arrhenius temperature

$$C_{P,\text{conf}} = C_{P,\text{liq}} - C_{P,\text{glass}} = C_{P,\text{liq}} - 3R. \quad (16)$$

Equation 16 is a consequence of the already-mentioned observation by Haggerty et al. (1968) that the heat capacity of oxide glasses reaches a limiting value of  $3R/(\text{g}\cdot\text{atom}\cdot\text{K})$  in the vicinity of the glass transition. At  $T \gg T_g$ , the application of the approximation (Eq. 16) is difficult to justify because at high temperatures configura-

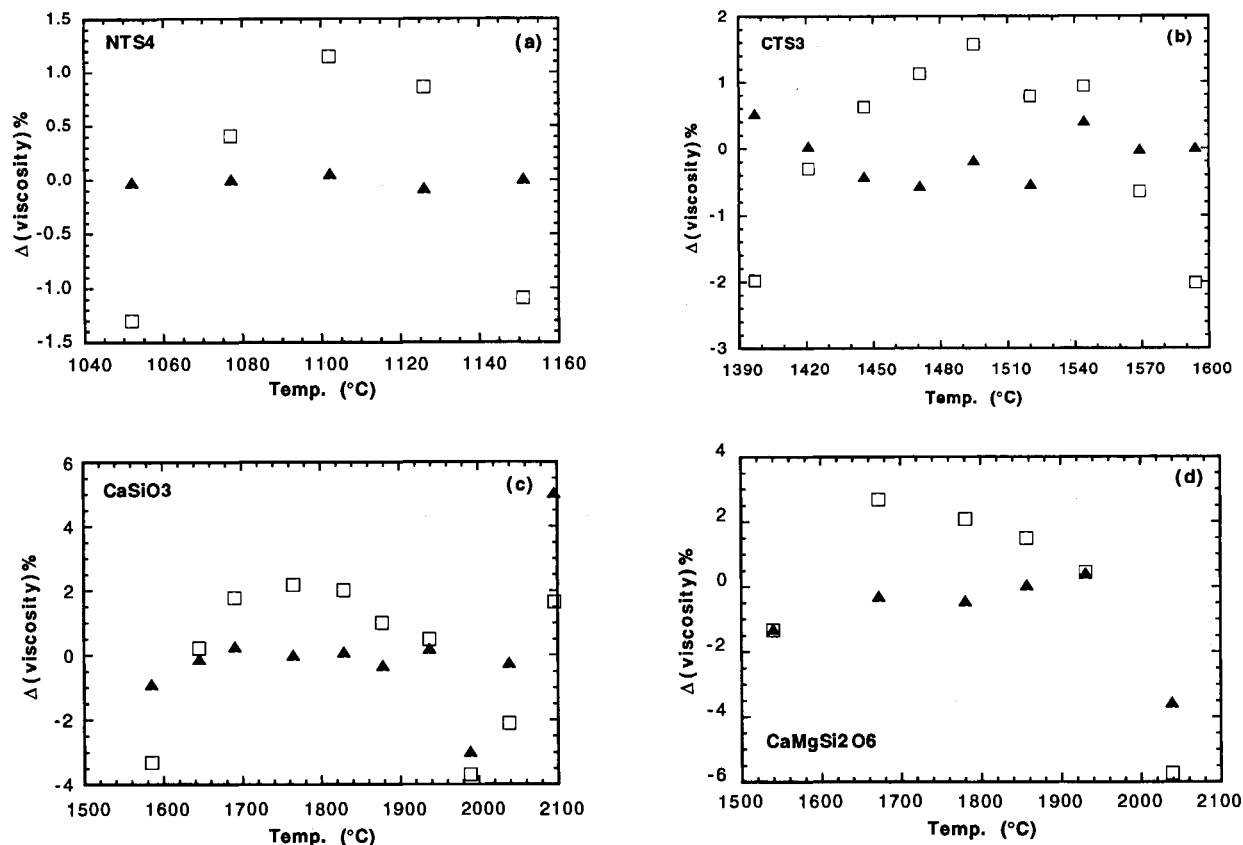


Fig. 7. The relative difference in percent between fits to viscosity measurements and the measured values. The open squares indicate deviations from Eq. 1; the solid triangles are for deviations from Eq. 9; for (a)  $(\text{Na}_2\text{SiO}_3)_{0.73}(\text{TiO}_2)_{0.27}$ ; data from Dingwell (1992); (b)  $(\text{CaSiO}_3)_{0.82}(\text{TiO}_2)_{0.18}$ ; data from Dingwell (1992); (c)  $\text{CaSiO}_3$ ; data from Urbain et al. (1982); (d)  $\text{CaMgSi}_2\text{O}_6$ ; data from Urbain et al. (1982).

dependences for the viscosities of several geologically important silicate liquids. Since then, much work has been done and published on liquid silicate viscosity, and among the geologically oriented contributions one should note Neuville and Richet (1991), Taniguchi (1992), Hummel and Arndt (1985), and Tauber and Arndt (1986, 1987), who unanimously demonstrated the inability of the Arrhenius equation to reproduce their observations in the intermediate viscosity regime. Also indispensable for geological applications are the observations on melts containing volatiles (Persikov et al., 1990) and on melts under pressure (Kushiro, 1980), but these topics were not considered here for space reasons.

At this moment not enough information is available for identification of the mass transport mechanisms operating in silicate glasses at  $T < T_g$ . In this respect, it would be very valuable if the pioneering measurements on the self-diffusion of O and Si in silicate melts by Shimizu and Kushiro (1984), Oishi et al. (1975), and Yinnon and Cooper (1980) were followed up by a systematic study on a well-characterized system. Another interesting source of information is the 2D NMR experiments done by Far-

nan and Stebbins (1990) on  $\text{K}_2\text{Si}_4\text{O}_9$ , and the system  $\text{SiO}_2\text{-Li}_2\text{O}$ . An extension to 4D experiments (Schmidt-Rohr and Spiess, 1991) of this work may contribute greatly to the identification of the flow mechanisms in amorphous silicates.

In this paper we have dealt exclusively with silicate liquids and glasses. One should be well aware that our discussion of the rheological properties was based to a large extent on the simplicities shown by the calorimetric observations, such that close to  $T_g$ ,  $C_{p,\text{glass}}$  attains its Dulong and Petit value. Moreover the excitation of configurational modes of freedom of silicate liquids seems to be less complicated than what has been observed in other liquids [see for example the work by Grimsditch and Toppell (1989) on  $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ ]. Therefore, our conclusions and recommendations are only meant to be relevant to silicate liquids.

The recognition of at least three different viscosity regimes should help to focus experiments designed to elucidate flow mechanisms in silicate liquids. Moreover, it cautions against indiscriminately extrapolating viscosity data.

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