American Mineralogist, Volume 88, pages 1390–1394, 2003

High-temperature limits on viscosity of non-Arrhenian silicate melts

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ABSTRACT

The prediction of viscosity in silicate melts, over the range of conditions found in nature, remains one of the most challenging and elusive goals in Earth Sciences. We present a strategy for fitting non-Arrhenian models [e.g., Vogel-Tammann-Fulcher (VTF) or Adam-Gibbs (AG)] to viscosity data that can be employed toward a full multicomponent model for melt viscosity. Our postulate is that the high-*T* viscosities of silicate melts converge to a common value. The implications are twofold. First, the number of composition-dependent parameters is reduced by a third. Second, our optimization constrains the experimentally inaccessible, high-*T* properties of silicate melts. The high-*T* limits to melt viscosity are constrained by the VTF and AG models to between $10^{-4.3\pm0.74}$ and $10^{-3.2\pm0.66}$ Pa·s, respectively, and overlap in the interval $10^{-3.86}$ to $10^{-3.56}$ Pa·s.

INTRODUCTION

It is 30 years since the first models for predicting the viscosity (η) of silicate melts as a function of melt composition and temperature were published (Bottinga and Weill 1972; Shaw 1972). These models are still used regularly to provide estimates of melt viscosity in studies concerning magmatism, volcanism, and planetary differentiation. The early models adopted an Arrhenian temperature dependence:

$$\log \eta = \frac{\alpha}{T(K)} + \beta \qquad (1)$$

where the two adjustable model parameters (α and β) vary with melt composition. The Arrhenian assumption was fully consistent with the available data; however, the current database of viscosity measurements covers a substantially wider range of melt compositions and temperatures (e.g., Richet and Bottinga 1995; Dingwell 1995). The new data require that future viscosity models accommodate strong non-Arrhenian temperature dependencies (Richet 1984; Hummel and Arndt 1985; Angell 1991; Rossler et al. 1998; Toplis et al. 1997). Recently, several new models have been published (Prusevich 1988; Persikov 1991; Baker 1996; Hess and Dingwell 1996; Giordano and Dingwell in press), but they are limited by using an Arrhenian formulation (e.g., Prusevich 1988; Persikov 1991) or by having compositional restrictions (Baker 1996; Hess and Dingwell 1996).

The main challenge to creating new models for viscosity in natural silicate melts is deciding how to partition the effects of composition across the parameters in the non-Arrhenian equation (Hummel and Arndt 1985; Toplis et al. 1997; Russell et al. 2002). We present a numerical analysis of fitting non-Arrhenian models to viscosity data for a variety of multicomponent silicate melts. Our results strongly support the premise that the high-temperature limiting behavior of all silicate melts can be approximated by a single common value of viscosity. This result greatly simplifies the task of modeling the compositional dependence of viscosity. Our analysis also provides estimates on the high-*T* behavior of silicate melts at conditions that are inaccessible experimentally.

SYNTHETIC MELTS: AN-AB-DI

The Vogel-Tammann-Fulcher (VTF) equation offers a purely empirical means of accommodating the non-Arrhenian temperature dependence of viscosity (Richet and Bottinga 1995; Rossler et al. 1998; Angell 1991; Bottinga et al. 1995):

$$\log \eta = A_{\mathrm{VTF}} + \frac{B_{\mathrm{VTF}}}{T(K) - C_{\mathrm{VTF}}} \qquad (2)$$

It is an effective descriptor of viscosity over the compositional range of most geochemically important melts (i.e., those showing relatively small departures from Arrhenian behavior) (Angell et al. 2000). The adjustable parameters ***A***, ***B***, and ***C*** depend on melt composition, but we expect these parameters to have different degrees and forms of compositional dependence. The parameter ***A*** is the value of log η (Pa·s) at infinite temperature, and ***C*** is the temperature (K) at which viscosity becomes infinite. The parameter ***B*** corresponds to the pseudo-activation energy associated with viscous flow, and is thought to represent a potential energy barrier obstructing the structural rearrangement of the melt. The parameters ***A***, ***B***, and ***C*** show strong correlations that are a reflection of: (1) the nonlinear nature of the VTF equation; (2) the distribution and quality of the experimental data; and (3) (potentially) co-dependence on composition (e.g., Russell et al. 2002). However, it can be difficult to isolate the compositional effects because of the strong numerical correlations.

We began by fitting the VTF equation to experimental data for 3 melt compositions having significantly different rheolo-

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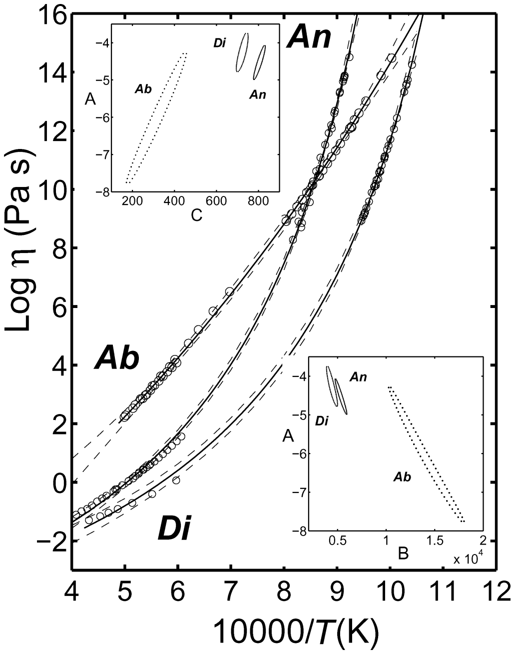

FIGURE 1. Optimal VTF equations (solid lines) fitted to individual viscosity datasets for diopside (Di), anorthite (An), and albite (Ab) melts (Table 1). Dashed lines represent the limits to the family of model VTF functions that are consistent with the 99% confidence limits on parameters $\boldsymbol{A}$, $\boldsymbol{B}$, and $\boldsymbol{C}$. (see insets; Russell et al. 2002).

gies (Fig. 1): albite (Ab), anorthite (An), and diopside (Di). Albite is a "strong" liquid[1] having near-Arrhenian behavior whereas diopside is more fragile and shows substantial non-Arrhenian temperature dependence. The optimal fits to the individual data sets (Table 1) describe the data well, and calculated confidence limits (99%) are used to map the resulting uncertainties and correlations on the model parameters (Insets, Fig. 1). The confidence envelopes depict the range of model values that, when combined in a non-arbitrary way, can reproduce the experimental data accurately. The confidence ellipses for individual melt compositions show that the model-induced correlations are substantial (e.g., Russell et al. 2002). This feature serves to caution us against attributing apparent correlations between model parameters (e.g., $\boldsymbol{A}$, $\boldsymbol{B}$, and $\boldsymbol{C}$) solely to variations in melt composition (e.g., Toplis 1998; Giordano and Dingwell in press).

Melts that are fragile and show strong non-Arrhenian behavior (Di and An) tightly constrain the values of the model parameters and generate relatively small confidence ellipses. Experimental data on strong liquids (Ab) show Arrhenian-like behavior (e.g., linear) and allow for a substantially larger range of parameter values in the VTF equation (Insets, Fig. 1). The 3 melt compositions define unique values of $\boldsymbol{B}$ and $\boldsymbol{C}$; however, the confidence limits on $\boldsymbol{A}$ for each melt are overlapping. The implication is that all three melts could share a common value of $\boldsymbol{A}$.

TABLE 1. Fits of VTF and AG equations to T(K)-log η datasets for diopside (Di, n = 39), anorthite (An, n = 57), and albite (Ab, n = 45) melts

	Individual Fitting			Global Fitting		
	Di	An	Ab	Di	An	Ab
A_{VTF}	−4.24	−4.5	−5.76	−4.46		
B_{VTF}	4367	5297	13299	4591	5246	10690
C_{VTF}	725	807	337	715	809	437
χ^2	6	27	4	8	27	12
A_{AG}	−3.34	−3.51	−4.34	−3.47		
B_{AG}	2292	2819	13628	2379	2784	10028
C_{AG}	703	778	186	696	781	275
χ^2	3	21	5	4	21	8

Notes: Sources are Di = Urbain et al. (1982), Sipp et al. (2001); An = Urbain et al. (1982), Scarfe et al. (1983), Hummel and Arndt (1985), Sipp et al. (2001); Ab = Urbain et al. (1982), Hummel and Arndt (1985), Scarfe and Cronin (1986), Sipp et al. (2001). Uncertainties on viscosity data are assumed as ≤ ± 0.2 log units.

This premise was tested by fitting the three data sets simultaneously to the VTF equation and solving for values of $\boldsymbol{B}$ and $\boldsymbol{C}$ for each melt and a single common value for $\boldsymbol{A}$ (Fig. 2A). The results of the optimization are statistically indistinguishable from the fits achieved on the individual data sets (Table 1, Fig. 2A) despite requiring the individual melts to share a common value of viscosity at high T (e.g., $\boldsymbol{A}_{\mathbf{VTF}} = 10^{-4.46 \pm 0.44}$).

An alternative means of describing the non-Arrhenian rheology of silicate melts is the Adam-Gibbs (AG) model, which is based on the configurational entropy (S^{conf}) theory of cooperative relaxation (Adam and Gibbs 1965). One attribute of this model is that it relates viscosity to the thermodynamic properties of silicate melts (Richet 1984; Bottinga et al. 1995; Richet and Bottinga 1995; Toplis et al. 1997). The AG model can be written in terms of 3 adjustable parameters that vary with melt composition:

$$\log = A_{\mathrm{AG}} \frac{B_{\mathrm{AG}}}{T \log\left\langle \dfrac{T}{C_{\mathrm{AG}}} \right\rangle} \tag{3}$$

under the conditions that the configurational heat capacity of the melt is constant and that S^{conf} vanishes to zero at some lower temperature (Richet 1984; Angell 1991; Toplis et al. 1997). The parameter $\boldsymbol{C}$ is the temperature at which S^{conf} becomes zero and viscosity goes to infinity. Under these conditions, the VTF and AG equations are operationally equivalent (Richet and Bottinga 1995; Angell 1991; Bottinga et al. 1995; Toplis et al. 1997).

We have taken a similar approach to fitting the AG model to the An-Ab-Di data set. The optimization, based on a single common unknown value of $\boldsymbol{A_{AG}}$, reproduces the experimental data exceptionally well, despite using two fewer adjustable parameters ($\boldsymbol{A_{AG}} = -3.47 \pm 0.37$; Fig 2B). In fact, there is no appreciable difference in the quality of fit relative to the individually fitted functions (Table 1). Mathematically, the concept of a common high-T limit to silicate melt viscosity is valid

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[1] The fragility of melts is a concept originally developed by Angell in the 1960s. Melt properties range from "fragile" (highly non-Arrhenian) to "strong" (near-Arrhenian), with some melts obviously exhibiting "intermediate" behavior.

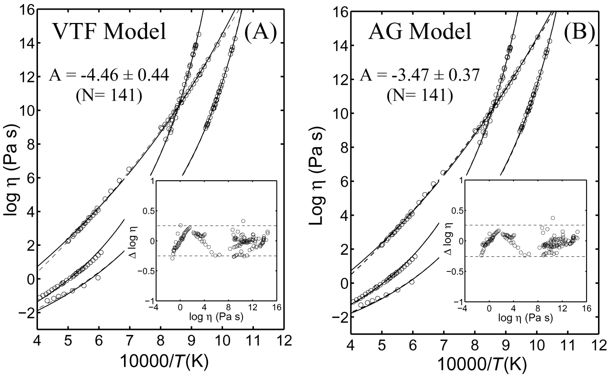

FIGURE 2. The entire Ab-An-Di dataset is fit to: (**A**) VTF or (**B**) Adam-Gibbs equations assuming that all 3 melt compositions share a common (but unknown) value of $\boldsymbol{A}$. Main figures compare the optimized functions employing a constant $\boldsymbol{A}$ (solid lines) to fits derived for individual melts (dashed lines). Insets show the level of misfit in values of log η predicted from the global optimization. Dashed lines denote ±0.25 log units of viscosity.

regardless of the model adopted (VTF vs. AG); however, the value of $\boldsymbol{A}$ is partly model dependent (e.g., –4.46 vs. –3.47).

NATURAL SYSTEMS

Ultimately a predictive model for viscosity must span the compositional and temperature ranges found in natural melts. Therefore, we have extended the analysis to include a set of 333 viscosity experiments performed on 20 (n) different anhydrous silicate melt compositions (Giordano and Dingwell in press). The experimental data span much of the compositional range found in natural systems, and include both near-Arrhenian and strongly non-Arrhenian melts (Fig. 3). Our optimization uses the full data set and provides estimates on 41 ($2n + 1$) parameters: values of $\boldsymbol{B}$ and $\boldsymbol{C}$ for each melt and a single estimate of $\boldsymbol{A}$. The optimized value for $\boldsymbol{A}_{\mathbf{VTF}}$ is –4.31 ± 0.74. The original data are reproduced to within error (≈± 0.2 log units; Inset Fig. 3), strongly corroborating our assertion of a common high-T limit for all silicate melts. Values of $\boldsymbol{B}_{\mathbf{VTF}}$ and $\boldsymbol{C}_{\mathbf{VTF}}$ for the 20 melt compositions vary between 4000 and 12 000, and between 275 and 700, respectively (Fig. 4). Although the values of $\boldsymbol{B}$ and $\boldsymbol{C}$ are strongly dependent on composition, much of the negative correlation shown in Figure 4 is numerical in character (Russell et al. 2002) reflecting the form of the VTF (or AG) function. Adopting the AG model, the same data constrain the optimal value of $\boldsymbol{A}_{AG}$ to be –3.15 ± 0.66, and the corresponding values of $\boldsymbol{B}_{AG}$ and $\boldsymbol{C}_{AG}$ span 2000 to 12 000 and 100 to 700, respectively.

The results of this analysis should enable us to realize a more robust model for predicting viscosity in non-Arrhenian multicomponent silicate melts. The optimization based on a single unknown value of $\boldsymbol{A}$ generates model curves that are indistinguishable from those achieved by fitting data sets individually (e.g., Figs. 1, 2, and 3). In essence, the available data cannot distinguish between a ($3n$)-parameter model and a ($2n + 1$)-parameter model. Operationally, this result means that the compositional dependence of viscosity can be restricted to only two ($\boldsymbol{B}$ and $\boldsymbol{C}$) of the three parameters in the non-Arrhenian

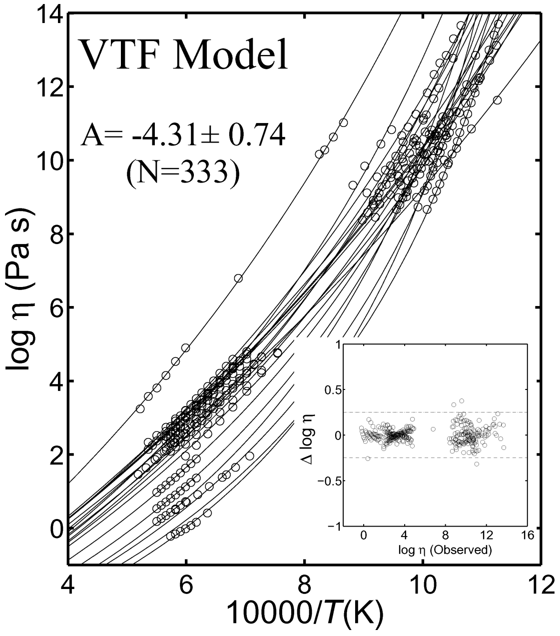

FIGURE 3. Measured values of viscosity for 20 multicomponent silicate melts (Giordano and Dingwell 2002) are fit simultaneously to model VTF curves (solid lines). Optimization uses a total of 333 experimental data and assumes that there is a single common value of $\boldsymbol{A}$ (–4.31 ± 0.74). Inset shows magnitude of deviations between measured and predicted values of log η.

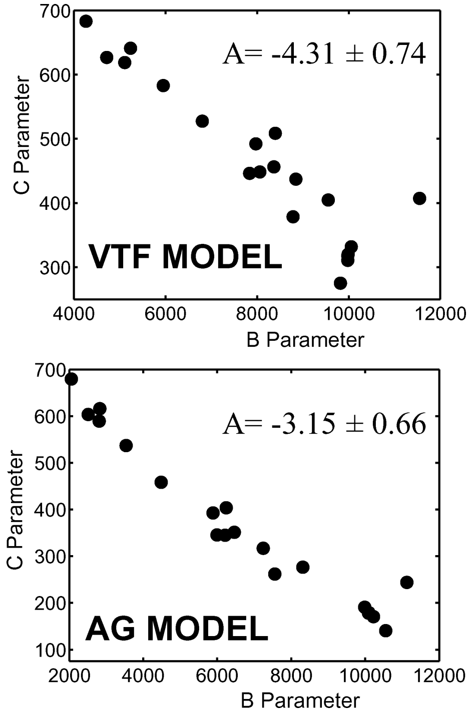

FIGURE 4. Comparison of models based on Vogel-Tammann-Fulcher (VTF) vs. Adam-Gibbs (AG) equations (see text) in terms of optimized parameters $\boldsymbol{B}$ and $\boldsymbol{C}$ for 20 multicomponent silicate melts (Fig. 3). Each optimization fits the model equations to 333 viscosity measurements, and assumes a single common value of $\boldsymbol{A}$.

model. This result simplifies the task of predicting viscosity in multicomponent silicate melts by reducing the number of compositionally dependent parameters by about one-third.

DISCUSSION

This analysis uses relatively low-*T* viscosity data to retrieve information on the high-*T* behavior of silicate melts, and suggests that non-Arrhenian and near-Arrhenian melts converge to a common viscosity at high *T* (Fig. 5). Conversely, if silicate melts truly have different high-*T* properties (e.g., ***A*** values), the relatively low-*T* experimental data cannot actually discern these differences. It is worth noting that the concept of a high-*T* limit to melt viscosity is implicit in the Arrhenian model of Shaw (1972) for silicate melt viscosities. In that model, high-*T* limits to viscosity are predicted by the relationship $\ln \eta_0$ (poise) = $-(1.5\ \boldsymbol{m} + 6.4)$, where ***m*** is a composition-dependent variable. However, calculations for a wide variety of melts ($2 < \boldsymbol{m} < 4$) yield a remarkably narrow range of high-*T* viscosity values (10^{-5} to 10^{-6} Pa·s).

The viscous properties of silicate melts cannot be studied directly at these temperatures which prompts the question: Is our optimized value of ***A*** a "*physically intelligible parameter*" (Angell et al. 2000)? We argue that the result does make physical sense. At temperatures well above liquidus conditions, all silicate melts will become highly dissociated liquids regardless of their structure at subliquidus temperatures. Indeed, there is no direct evidence to suggest that "fragile," "intermediate" and, even, "strong" silicate melts (as defined in the footnote on page 4) maintain different rheologies at temperatures well above their respective glass transition temperatures (T_g) (Angell 1991; Angell et al. 2000). The implication is that silicate melts, as diverse as basalt and rhyolite, should converge to a common high-*T* limiting value of viscosity.

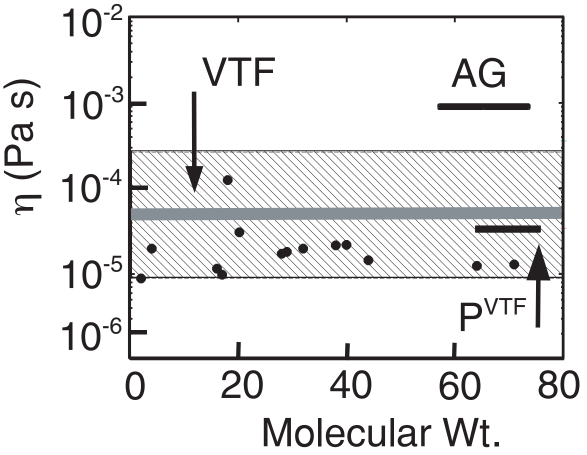

FIGURE 5. Values of η for common gases (H_2, He_4, CH_4, NH_3, H_2O, Ne, CO, N_2, Air, O_2, F_2, Ar, CO_2, SO_2, Cl_2) at 17–25 °C (except H_2O at 100 °C) are plotted against molecular weight (solid dots) and compared to predicted high-*T* viscosity limits for silicate melts. All gases have ambient values of log η between –5.2 and –4. Patterned area denotes 99% confidence limits on ***A*** from fitting 20 silicate melts simultaneously to VTF function (–4.31). The confidence limits enclose the value of ***A*** obtained for the Ab-An-Di melt system ($P^{VTF} = -4.46$). AG denotes the value of ***A*** (–3.15) obtained by fitting the Adam-Gibbs model to the natural melt system.

The concept of a high-*T* limit to silicate melt viscosity (e.g., constant ***A***) is supported by considering the time scales of relaxation processes in melts (Richet and Bottinga 1995; Angell 1991; Angell et al. 2000). The Maxwell relationship ($\tau = \eta_0 / G\infty$) can be used to constrain the lower limits to melt viscosity (η_0). The bulk shear modulus ($G\infty$) of the melt at infinite frequency can be assigned an average value of ~10^{10} Pa (Toplis 1998; Dingwell and Webb 1989). The relaxation time scale (τ) of the melt is dictated by the quasilattice vibration period (~10^{-14} s), which represents the time between successive assaults on the energy barriers to melt rearrangement (Angell 1991; Toplis 1998; Angell et al. 2000). Thus, the lower limiting value to viscosity (η_0) should approximate 10^{-4} Pa s. Allowing for some variation in these physical constant, would still restrict ***A*** to ±1 units and establish the high-*T* viscosity limits for melts at between $10^{-3.5}$ and $10^{-5.5}$ Pa·s (Toplis 1998; Angell et al. 2000).

The value of ***A*** constrained by low-*T* viscosity data partly depends on the model adopted (Fig. 5). The VTF model applied to synthetic and natural melts returns estimates for the high-*T* limits on silicate melt viscosity that are within experimental error of each other (e.g., $10^{-4.5}$ vs. $10^{-4.3}$). The AG model applied to the same two data sets also returns identical values ($10^{-3.5}$ vs. $10^{-3.2}$). However, the values of ***A*** predicted by the two models differ systematically, with $\boldsymbol{A}_{\mathbf{VTF}}$ being ≈1 log unit less than $\boldsymbol{A}_{\boldsymbol{AG}}$. This result reflects the fact that ***A*** is derived by extraoplation of the model well beyond the range of measurements and the models use fundamentally different equations for the extrapolation (e.g., Bottinga et al. 1995). Given these considerations, the values of ***A*** derived from the VTF ($10^{-4.3 \pm 0.74}$) and AG ($10^{-3.2 \pm 0.66}$) models show remarkable agreement. Indeed, the two estimates of ***A*** overlap and agree at the 99% confidence level; the optimal value of ***A*** lies in the interval –3.57 to –3.81.

These estimates of ***A*** represent robust and independent estimates for the high-*T* limits to silicate melt viscosity and roughly coincide with the viscosities reported for common gases at ambient conditions (Fig. 5; mean value of $10^{-4.7}$ Pa·s). Our results are also generally consistent with observations from many low-*T* glass-forming systems (Angell 1991). In those systems, experiments can be run at temperatures that are well above the corresponding values of T_g (e.g., $T_g/T \rightarrow 0$) and, thus, can directly explore the high-*T* properties of melts. These experiments have shown that, at temperatures well above T_g, both "strong" and "fragile" melts commonly converge to a common viscosity (e.g., 10^{-5} Pa·s; Angell 1998; 1991; Angell et al. 2000).

ACKNOWLEDGMENTS

This research was supported by the Natural Sciences and Engineering Research Council of Canada (J.K. Russell) and by the International Quality Networks grants program (D. Dingwell). The manuscript benefited from critical reviews by M. Toplis, J. deClaville Christiansen, and an anonymous reviewer.

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MANUSCRIPT RECEIVED DECEMBER 19, 2002
MANUSCRIPT ACCEPTED MAY 12, 2003
MANUSCRIPT HANDLED BY SIMON KOHN