

# Viscosity of hydrous rhyolitic melts inferred from kinetic experiments, and a new viscosity model

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## ABSTRACT

Viscosity of hydrous silicate melts is a critical property for understanding magma transport, bubble growth, volcanic eruption, and magma fragmentation. We report new inferred viscosity for hydrous rhyolitic melt in the viscosity range of  $10^9$  to  $10^{15}$  Pa·s based on the kinetics of hydrous species reactions in the melt upon cooling (i.e., based on the equivalence between the glass-transition temperature and the apparent equilibrium temperature), as well as data from bubble-growth experiments. By combining viscosity data of rhyolitic melts containing from 6 ppm to about 8.0 wt% total H<sub>2</sub>O (both our own data and literature data), we propose the following relation for the dependence of viscosity on total H<sub>2</sub>O content at a given temperature and pressure:

$$\frac{1}{\eta} = \frac{1}{\eta_1} + \left(\frac{1}{\eta_2} - \frac{1}{\eta_1}\right)x^n \approx \frac{1}{\eta_1} + \frac{1}{\eta_2}x^n$$

where  $\eta$  is viscosity and  $1/\eta$  is fluidity,  $\eta_1$  is the viscosity of the dry melt,  $x$  is the mole fraction of total dissolved H<sub>2</sub>O,  $n$  and  $\eta_2$  are two fitting parameters, and  $\eta_2$  can be interpreted to be the viscosity of the hypothetical melt consisting of pure H<sub>2</sub>O. The above simple equation appears to work well in modeling viscosity of hydrous rhyolitic melts. Using the above functional form and a weighted nonlinear regression, experimental data covering 570 to 1920 K and 0.0006 to 8.2 wt% total H<sub>2</sub>O are used to obtain the following non-Arrhenian model for the viscosity of Mono Crater rhyolitic melts:

$$\log \eta = -\log \{ \exp(18.5611 - 49584/T) + \exp[1.47517 - (1795.5/T)^{1.9448}]x^{1 + (1812.2/T)^2} \}$$

where  $T$  is in K, and  $x$  is the mole fraction of total dissolved H<sub>2</sub>O on a single oxygen basis. The  $2\sigma$  uncertainty in the above 6-parameter formula is 0.36 in terms of  $\log \eta$  (for experimental data with errors smaller than 1 log unit), much less than uncertainties in all previous models for hydrous rhyolitic melt. We hence recommend its use for predicting the viscosity of high-SiO<sub>2</sub> and calc-alkaline rhyolitic melts.

Our model shows that a minute H<sub>2</sub>O content can still affect the melt viscosity significantly, especially at low temperatures (i.e., high viscosity). For example, at 973 K, the viscosity of rhyolitic melt increases by 1.2 orders of magnitude from a melt with 0.1 wt% total H<sub>2</sub>O to a melt with less than 100 ppm total H<sub>2</sub>O. Because a nominally “dry” melt may still contain some H<sub>2</sub>O, such as several hundred ppm, it is critical for experimentalists to report its total H<sub>2</sub>O content for viscosity measurements. Some inconsistency in literature viscosity data might be attributable to small variations in H<sub>2</sub>O content in the samples.

## INTRODUCTION

Viscosity of hydrous silicate melts is essential in modeling the dynamics of magma transport and volcanic eruptions. Numerous experimental measurements of viscosity, as well as viscosity models, have been published. For general melt compositions, the classic models of either Bottinga and Weill (1972) or Shaw (1972) are still used, not because they are reliable, but because of the extreme difficulty in calibrating something better (Lange 1994). For specific melt compositions, more advanced models and relations have been developed (e.g., Richet 1984; Richet et al. 1986, 1996; Hess and Dingwell 1996; Scaillet et al. 1996; Schulze et al. 1996; Dingwell et al. 1998a,

1998b, 2000; Holtz et al. 1999; Hess et al. 2001; Romano et al. 2001; Whittington et al. 2000, 2001). For example, Hess and Dingwell (1996) presented a much-improved viscosity model for hydrous granitic melts, covering a large range of temperatures and water contents.

Although much progress has been made, the accuracy of calculated melt viscosity from viscosity models is not enough for the purpose of modeling magma dynamics or various component processes in volcanic eruptions. Even the models for specific melt compositions still need further improvement. For example, the viscosity model of Hess and Dingwell (1996) has a  $2\sigma$  uncertainty of 0.92 in terms of  $\log \eta$ , meaning that viscosity only can be calculated to within a factor of 8. Such an uncertainty is too large for modeling magmatic processes like bubble growth. Liu and Zhang (2000) acquired experimental

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data on bubble growth in rhyolitic melt at 500–600 °C, and compared the experimental data with calculations using the program of Proussevitch and Sahagian (1998). The calculation requires expressions of melt viscosity (Hess and Dingwell 1996), and H<sub>2</sub>O solubility (Zhang 1999b) and diffusivity (Zhang and Behrens 2000) in the melt. Liu and Zhang (2000) concluded that calculated bubble-growth rates can be brought into perfect agreement with experimental data if the viscosity of Hess and Dingwell (1996) is decreased by a factor of 1.3 to 4 on average (adjusting other input parameters within their uncertainty does not help much). Hence, improving viscosity data and the viscosity model is a key for understanding bubble growth, which is a critical process for magma fragmentation (Zhang 1999a) and volcanic eruption. It is also crucial for a general understanding of magma-flow dynamics, as well as melt relaxation and glass transition.

Common experimental methods for determining viscosity of silicate melts can be classified into two categories: those for low viscosity (0.1–10<sup>6</sup> Pa·s), and those for high viscosity (10<sup>8.5</sup>–10<sup>13</sup> Pa·s). The methods for measurement of low viscosities include the concentric cylinder viscometer at one atmosphere (e.g., Dingwell 1986) and the falling sphere technique (e.g., Shaw 1963). The methods for measurement of high viscosities include the micropenetration method at one atmosphere (e.g., Hummel and Arndt 1985) and the parallel plate creep method (e.g., Neuville and Richet 1991). The falling sphere technique has been improved with the assistance of a centrifuge to measure viscosities up to 10<sup>8</sup> Pa·s (Dorfman et al. 1996). The parallel plate creep technique has been adapted for high-pressure viscosity measurements (Schulze et al. 1999). Because magmatic processes occur at both low and high viscosities, and because extrapolation from either end to the other would produce large uncertainties due to the non-Arrhenian behavior of viscosity, it is essential to determine viscosities experimentally at both high and low viscosities.

We describe a new method for inferring viscosity based on controlled cooling-rate experiments on hydrous rhyolitic melt. This method is based on the equivalence between the rheologically defined glass-transition temperature ( $T_g$ ) and the chemically defined apparent equilibrium temperature ( $T_{ac}$ ) of the hydrous species reaction at a given cooling rate. The method may be used to infer viscosities in the range of 10<sup>9</sup> to 10<sup>15</sup> Pa·s. It requires an understanding of speciation and reaction kinetics of dissolved H<sub>2</sub>O in silicate melts. Such an understanding is gained through work in this and other labs over the past several years. Below, we explain the principles for viscosity inference, report experimental data, and compare data from different methods to assess the equivalence between  $T_g$  and  $T_{ac}$ . Combining our data with those from the literature, we examine the dependence of viscosity on H<sub>2</sub>O content, and develop a new model for the viscosity of hydrous rhyolitic melt.

#### PRINCIPLES OF INFERRING VISCOSITY FROM CONTROLLED COOLING RATE EXPERIMENTS

Before reviewing the principles, some definitions are in order. H<sub>2</sub>O is used to refer to the H<sub>2</sub>O component dissolved in a melt. It is known that when H<sub>2</sub>O dissolves in a silicate melt, part of it reacts with the melt to form OH. That is, there are at

least two distinguishable species of dissolved H<sub>2</sub>O: one is molecular H<sub>2</sub>O (hereafter referred to as H<sub>2</sub>O<sub>m</sub>), and the other is hydroxyl group XOH where X is a cation other than H (referred to as OH). Total H<sub>2</sub>O content will be referred to as H<sub>2</sub>O<sub>t</sub>. In silicate melts, H<sub>2</sub>O<sub>m</sub> is characterized by an infrared (IR) band at 5230 cm<sup>-1</sup>, and OH is characterized by an IR band at 4520 cm<sup>-1</sup> (Stolper 1982a, 1982b). From these bands, the hydrous species concentrations can be determined quantitatively by infrared spectroscopy as long as molar absorptivities are calibrated.

The inference of melt viscosity is based on the kinetics of the following reaction:



where O is anhydrous oxygen. The equilibrium constant  $K$  is defined as:

$$K = \frac{(\text{OH})^2}{(\text{H}_2\text{O}_m)(\text{O})} \quad (2)$$

where brackets mean activities approximated by mole fractions. The equilibrium and kinetics of the reaction in rhyolitic melt have been studied extensively (Stolper 1982a, 1982b; Silver and Stolper 1989; Silver et al. 1990; Dingwell and Webb 1990; Ihinger 1991; Zhang et al. 1991, 1995, 1997a, 1997b; Ihinger et al. 1999; Withers et al. 1999; Zhang 1999b; Nowak and Behrens 2001). Because there are still uncertainties in the molar absorptivities of the IR bands (e.g., Zhang et al. 1997a), the relationship between  $K$  and temperature is cast in terms of band intensities as follows (Ihinger et al. 1999):

$$\ln \frac{A_{452}^2}{A_{523}} = a_0 + \frac{1000}{T} (b_0 + b_1 A_{523} + b_2 A_{452}) \quad (3)$$

where  $A_{523}$  and  $A_{452}$  are the absorbances (peak heights) for the 5230 and 4520 cm<sup>-1</sup> bands per mm sample thickness,  $A_{452}^2/A_{523}$  is a proxy for  $K$ ,  $T$  is in kelvin (K),  $a_0 = 2.482$ ,  $b_0 = -2.660$ ,  $b_1 = -0.0896$ , and  $b_2 = -1.082$  for rhyolite. The absorbances are relative to a flexicurve baseline (e.g., Zhang 1999b) instead of a linear baseline. The above equation is independent of any knowledge of the molar absorptivities and the actual H<sub>2</sub>O<sub>m</sub> and OH concentrations, and it can reproduce experimental temperature with a 2σ uncertainty of 13 K directly from measured absorbances. Note that the debate on quenched vs. *in situ* speciation studies has been resolved (Withers et al. 1999; Nowak and Behrens 2001; Behrens and Nowak 2003), and the conclusion is that species concentrations do not change below the glass-transition temperature.

To infer viscosity, a hydrous silicate melt is heated to a high temperature to reach species equilibrium. To avoid bubbling, the experiment is best done under pressure (using a piston-cylinder apparatus or a cold-seal pressure vessel), although one-bar experiments also can be carried out at low H<sub>2</sub>O. After heating, the sample is cooled at a desired rate to room temperature. After doubly polishing the quenched glass sample (hence removing the dehydrated layers), the IR spectrum is taken. The band intensities ( $A_{523}$  and  $A_{452}$ ) in the quenched glass are measured with FTIR, and then a temperature is calculated from Equation 3. For a continuously cooled melt, the final species concentrations in the quenched glass were not attained

through equilibrium at any single temperature (Zhang 1994). Hence, the calculated temperature is referred to as the *apparent* equilibrium temperature  $T_{ac}$  (Zhang 1994). The basic principle for inferring viscosity is the equivalence of glass-transition temperature ( $T_g$ ) and  $T_{ac}$  (Dingwell and Webb 1990; Stevenson et al. 1995; Zhang et al. 1997b). That is, the viscosity at  $T_{ac}$  is

$$\eta|_{T_{ac}} = \eta|_{T_g} = 10^{11.45}/q \quad (4)$$

where  $\eta$  is viscosity,  $q$  is quench rate, and the unit of the constant  $10^{11.45}$  is Pa·K, so that when the quench rate  $q$  is in K/s, the unit of viscosity  $\eta$  is Pa·s. The  $2\sigma$  uncertainty in the value 11.45 is about 0.2 (to be discussed below). With the above definition, for a quench rate of 10 K/min,  $T_{ac}$  would be the temperature at which the viscosity is  $1.69 \times 10^{12}$  Pa·s.

From the assumed  $T_g \sim T_{ac}$  equivalence, the key in this method to inferring viscosity from a controlled cooling-rate experiment is not to find the viscosity, but the temperature ( $T_{ac}$ ). With  $T_{ac}$  calculated from the IR spectrum using Equation 3, a data point of viscosity at a given  $T$  and  $H_2O_i$  is obtained.

## EXPERIMENTS AND DATA

The starting materials include Mono Craters rhyolite (MCR) from California, and glass samples prepared by hydration of MCR. On an anhydrous basis, all the glass chips have identical chemical compositions as listed under MCR in Table 1.

Experimental data are from two studies of reaction kinetics (Zhang et al. 1997b, 2000) and experimental details can be found there. The experimental conditions and inferred viscosity are reported in Table 2. For  $T_{ac}$  determination, the  $2\sigma$  reproducibility is typically 4 K (Table 2), but the accuracy of Equation 3 is about 13 K (Ihinger et al. 1999), which means that there is room for improving the temperature calibration in the future. For  $H_2O_i$  determination, the precision is about 1% relative and the accuracy is about 0.15 wt% (depending on  $H_2O_i$ ). The data in  $\log q$  have a  $2\sigma$  accuracy of smaller than 0.02 units, but the accuracy to infer  $\log \eta$  depends on the accuracy of the  $T_g \sim T_{ac}$  equivalence (that is, the accuracy of the constant  $10^{11.45}$  in Equation 4; see Discussion).

Some viscosity data have been obtained from bubble-growth experiments (Liu and Zhang 2000). Liu and Zhang (2000) carried out bubble-growth experiments at 1 bar and 525–600 °C, with 1.3 to 2.1 wt%  $H_2O_i$ . By modeling and reproducing their bubble-growth data (e.g., Fig. 3 in Liu and Zhang 2000), the viscosity of the hydrous melt is extracted from each series of experiments. The data are listed in Table 3.

## DISCUSSION

### $T_g \sim T_{ac}$ equivalence

The equivalence between rheologically defined  $T_g$  and kinetically defined  $T_{ac}$  must be verified before it is used to infer the viscosity. Dingwell and Webb (1990) proposed the equivalence and used the viscosity model of Shaw (1972) to estimate  $T_{ac}$ . When studying the kinetics of Reaction 1, Zhang et al. (1995) concluded that if the viscosity model of Shaw (1972) were used, then  $T_g$  and  $T_{ac}$  would differ by 70–100 °C, indicating either the  $T_g \sim T_{ac}$  equivalence would not hold or the viscosity model of Shaw (1972) needed major improvement. Hess and Dingwell (1996) (referred to as H&D hereafter) presented a much-improved viscosity model for hydrous rhyolitic melt applicable to both high and low temperatures:

$$\log \eta = f(T, w) = [-3.545 + 0.833 \ln(w)] \\ + [9601 - 2368 \ln(w)] / \{T - [195.7 + 32.25 \ln(w)]\} \quad (5)$$

where  $w$  is  $H_2O_i$  content in wt% (for 1 wt%  $H_2O_i$ ,  $w = 1$ ) and  $T$  is temperature in K. H&D also compared their model with some other models and concluded that their model significantly improves the quality of fit over other models. With the H&D viscosity model, there is good agreement between  $T_g$  and  $T_{ac}$  (Zhang et al. 1997b), except for a very small systematic difference (Fig. 1). As shown by Figure 1, this systematic difference cannot be attributed solely to uncertainty in estimating  $T_{ac}$ , but can be attributed to either the arbitrariness of the rheological definition of  $T_g$ , or a small systematic error in the above viscosity model used to calculate  $T_g$ . Thus, the  $T_g \sim T_{ac}$  equivalence is verified. Other authors have verified the equivalence between volume, enthalpy, and viscosity relaxation (e.g., Toplis et al. 2001; Sipp and Richet 2002).

Because viscosity data are determined at various temperatures and  $H_2O_i$  concentrations, direct comparison of experimental viscosity data is sometimes not possible. To examine the effect of one parameter (such as  $H_2O_i$ ) on viscosity by fixing

**TABLE 1.** Rhyolitic and some haplogranitic melt composition on anhydrous basis (oxide wt%)

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Total	Si + Al <sup>T</sup>	Δ
MCR	76.59	0.08	12.67	1.00	0.03	0.52	3.98	4.88	99.75	0.846	≡0
Rhyolite1	76.6	0.10	12.7	1.08	0.03	0.31	4.1	4.6	99.52	0.847	≡0
EDF	77.18	0.09	12.91	0.61	0.07	0.51	4.05	4.52	99.94	0.847	≡0
BL6	77.99	0.17	12.25	1.22	0.17	1.08	3.66	3.39	99.93	0.840	≡0
Rhyolite2	77.90	0.07	12.05	0.76	0.05	0.52	4.01	4.06	99.42	0.854	≡0
Rhyolite3	74.16	0.07	12.02	1.22	0.08	0.35	3.73	4.77	96.4	0.848	≡0
LCO	76.37	0.11	13.35	0.76	0.07	0.51	4.31	4.67	100.2	0.841	–
AOQ	76.14	0	13.53	0	0	0	4.65	5.68	100	0.850	≡0
HPG8	78.6	0	12.5	0	0	0	4.6	4.2	99.9	0.863	0.20
GB4	72.94	0.06	15.57	0.74	0.14	0.57	4.56	4.14	98.72	0.814	–0.18
Rhyolite4	73.23	0.19	13.6	2.78	0.17	1.69	3.78	4.11	99.55	0.807	–0.57

*Notes:* MCR means Mono Crater rhyolite used in this work and the composition is from Zhang et al. (1997a). Source of other viscosity data and chemical composition data: Rhyolite1 is from viscosity study by Shaw (1963); Rhyolite2 by Neuville et al. (1993); Rhyolite3 by Friedman et al. (1963) with composition given in Shaw (1972) (note that when normalized to 100%, its composition is close to MCR); EDF and BL6 by Stevenson et al. (1995); AOQ (Qz28Ab38Or34) by Schulze et al. (1996) with composition from Holtz et al. (1992); LCO by Baker (1996); HPG8 by Hess et al. (1995); Dingwell et al. (1996) and Dorfman et al. (1996); GB4 by Scaillet et al. (1996) with analysis in Scaillet et al. (1995); Rhyolite4 by Persikov et al. (1990). Si+Al<sup>T</sup> is the cation mole fraction of Si plus Al associated with Na or K. Δ = average value of ( $\log \eta_{data} - \log \eta_{calc}$ ) where  $\eta_{calc}$  is calculated from our new model (see also Table 4).

**TABLE 2.** Viscosity data for hydrous rhyolitic melt from controlled cooling rate experiments

Sample	$q$ K/s	$P$ MPa	$A_{523}$ mm <sup>-1</sup>	$A_{452}$ mm <sup>-1</sup>	H <sub>2</sub> O <sub>i</sub> wt%	$T_{ae}$ K	log <sub>10</sub> $\eta$ with $\eta$ in Pa·s	Ref.
KS-C9	0.000177	0.1	0.0585	0.1224	0.809	728±3	15.20	1
2b-4C1	0.000177	0.1	0.179	0.173	1.57	671±3	15.20	1
7b-4C1	0.000177	0.1	0.335	0.208	2.39	643±2	15.20	1
KS-C6	0.00176	0.1	0.0576	0.129	0.839	752±4	14.20	1
KS-C4	0.00551	0.1	0.0556	0.130	0.839	765±4	13.71	1
5b5-C1	0.0165	0.1	0.0641	0.140	0.928	769±1	13.23	1
KS-C2	0.0165	0.1	0.0599	0.137	0.892	772±3	13.23	1
7b7-C1	0.0166	0.1	0.0202	0.095	0.513	841±4	13.23	1
2b7-C1	0.0167	0.1	0.201	0.202	1.82	709±3	13.23	1
2b3b1	0.0168	0.1	0.187	0.195	1.73	710±9	13.22	1
4b5-C1	0.0168	0.1	0.134	0.178	1.42	730±5	13.22	1
3b12-C1	0.0169	0.1	0.356	0.235	2.63	678±4	13.22	1
KS-C7	0.0178	0.1	0.0519	0.1314	0.831	784±1	13.20	1
KS-C8	0.0179	0.1	0.0534	0.132	0.840	779±2	13.20	1
KS-C3	0.0493	0.1	0.0472	0.131	0.811	804±3	12.76	1
3b12-C2	0.108	0.1	0.431	0.256	3.06	682±4	12.42	1
2b3a1	0.125	0.1	0.168	0.200	1.68	738±3	12.35	1
2b7-C3	0.130	0.1	0.196	0.210	1.86	731±4	12.34	1
4b5-C2	0.141	0.1	0.127	0.185	1.43	757±4	12.30	1
5b5-C2	0.150	0.1	0.0828	0.161	1.12	780±3	12.27	1
KS-C1*	0.161	0.1	0.0422	0.130	0.784	825±4	12.24	1
KS-C1*	0.161	0.1	0.0437	0.132	0.799	823±5	12.24	1
KS-C1*	0.161	0.1	0.0458	0.134	0.819	820±3	12.24	1
3b12-C3	0.546	0.1	0.399	0.267	3.00	710	11.71	1
4b5-C3	0.761	0.1	0.117	0.190	1.42	787±5	11.57	1
2b7-C4	0.823	0.1	0.189	0.218	1.88	755±3	11.53	1
5b5-C3	0.915	0.1	0.0805	0.169	1.16	810±4	11.49	1
3aD2A-C1	0.670	200	0.278	0.242	2.37	729±3	11.62	2
KS-C11	0.828	200	0.0445	0.138	0.839	846	11.53	2
KS-C12	6.5	200	0.0389	0.141	0.830	892	10.64	2
3b11-C	66	200	0.150	0.236	1.84	845±1	9.63	2
KS-C10	69	200	0.0298	0.140	0.791	971±8	9.61	2
KS&3-C4	0.00167	500	0.597	0.247	3.80	625±4	14.23	2
KS&7-C3	0.0162	500	1.266	0.268	7.70	573±3	13.24	2
KS&5-C3	0.0164	500	0.967	0.274	5.60	604±1	13.24	2
POB10-C1	0.0168	500	0.0926	0.158	1.14	748±10	13.22	2
KS&3-C3	0.0168	500	0.577	0.256	3.80	642±3	13.00	2
KS&7-C6	0.991	500	1.23	0.303	7.70	603±1	11.45	2
KS&5-C4	1.02	500	0.909	0.308	5.60	648±2	11.44	2
3aD2A-C2	59	500	0.264	0.278	2.55	804±4	9.68	2
KS&3-C2	68	500	0.482	0.315	3.80	750±1	9.62	2
KS&5-C2	70	500	0.838	0.350	5.60	707±2	9.60	2
KS&7-C2	71	500	1.15	0.354	7.70	670±4	9.60	2
POB10-C2	94	500	0.0669	0.182	1.17	897±4	9.48	2

Notes:  $q = -d\bar{T}/dt$  at  $T = T_{ae}$ ;  $A_{523}$  and  $A_{452}$  are absorbance per mm sample thickness (uncertainty is about 1% relative); H<sub>2</sub>O<sub>i</sub> is obtained using the calibration of Zhang et al. (1997a) for H<sub>2</sub>O<sub>i</sub> < 2.6 wt%, and from Karl-Fischer titration for higher H<sub>2</sub>O<sub>i</sub>;  $T_{ae}$  (K) = (2660 + 89.6 $A_{523}$  + 1082 $A_{452}$ )/[2.482 - ln( $A_{452}/A_{523}$ )] (Hinger et al. 1999);  $\eta = 10^{11.45}/q$  where the unit of  $10^{11.45}$  is Pa·K. The 2 $\sigma$  precision for  $T_{ae}$  from IR spectra is given if there are two or more spectra. The 2 $\sigma$  accuracy for  $T_{ae}$  is 13 K. Ref. 1 = Zhang et al. 1997b; 2 = Zhang et al. 2000. Although the uncertainty in log $q$  is  $\leq 0.02$ , the uncertainty in  $T_{ae}$  translates to an uncertainty of 0.2 in log $\eta$  (see text).

\* This sample is large and heterogeneous. Hence the data are divided in three groups according to H<sub>2</sub>O<sub>i</sub>.

**TABLE 3.** Viscosity data for hydrous rhyolitic melt from bubble-growth experiments

Sample	$T$ K	$P$ MPa	H <sub>2</sub> O <sub>i</sub> wt%	log <sub>10</sub> $\eta$ h in Pa·s
B1-1	873 ± 2	0.1	2.03 ± 0.20	8.72 ± 0.30
B1-2	798 ± 2	0.1	1.97 ± 0.20	10.30 ± 0.20
B1-3	773 ± 2	0.1	1.97 ± 0.30	10.82 ± 0.20
B1-5	848 ± 2	0.1	2.04 ± 0.20	9.26 ± 0.15
B1-6	824 ± 2	0.1	2.03 ± 0.20	9.68 ± 0.15
B2-1	873 ± 2	0.1	1.36 ± 0.25	9.70 ± 0.15
B2-C	848 ± 2	0.1	1.41 ± 0.2	10.30 ± 0.15
B3-1	873 ± 2	0.1	1.46 ± 0.2	9.62 ± 0.15

Notes: Data are extracted from the bubble-growth experiments of Liu and Zhang (2000). Only the averages are reported in this table. Individual viscosity points (from growth data of individual bubbles) are used in the weighted nonlinear regression.

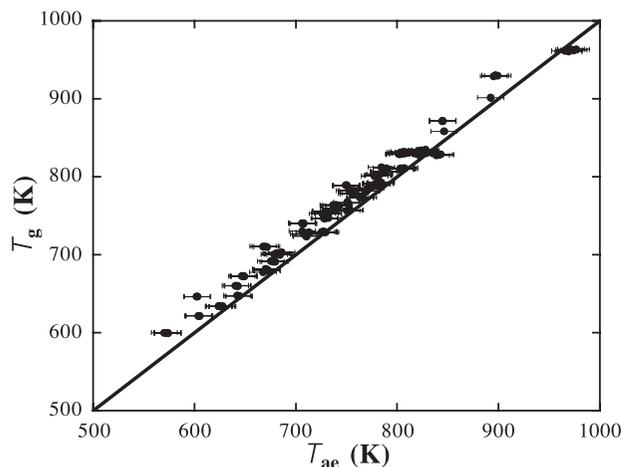
other parameters, we used the H&D formulation (Eq. 5) to make adjustments to viscosity data in a small temperature or H<sub>2</sub>O<sub>i</sub> range. For example, if the measurement is made at  $T_1$  and we need to estimate the viscosity at  $T_2$ , the following formula is

used to estimate log $\eta$  at  $T_2$ :

$$\log\eta(T_2, w) = \log\eta(T_1, w)_{\text{measured}} + f(T_2, w) - f(T_1, w) \quad (6)$$

where  $f(T, w)$  is the function given in Equation 5. As  $|T_2 - T_1|$  increases, the uncertainty in the viscosity estimation using Equation 6 also increases. Although we will argue later that H&D model is imperfect, we still expect that it can be applied to adjust viscosity values in a small temperature or H<sub>2</sub>O<sub>i</sub> range. Furthermore, we use the H&D model to adjust data so that any disagreement between adjusted data and the H&D model to be discussed later is not due to problems in adjusting the data.

Using the above procedure, we compare available viscosity data of rhyolitic melt at 823 ± 100 K in Figure 2a. For data at  $T \sim 823$  K, the viscosity data are adjusted using Equation 6 to the common temperature of 823 K for comparison. The constant in Equation 4 was chosen to be  $10^{11.45}$  so that the viscosity data



**FIGURE 1.** Comparison of calculated  $T_g$  (calculated from Hess and Dingwell 1996) and experimental  $T_{ae}$  for experimentally quenched hydrous rhyolitic melt. Data are shown as solid circles. The line is a 1:1 line. Error bars (at  $2\sigma$  level) for estimating  $T_{ae}$  are shown.

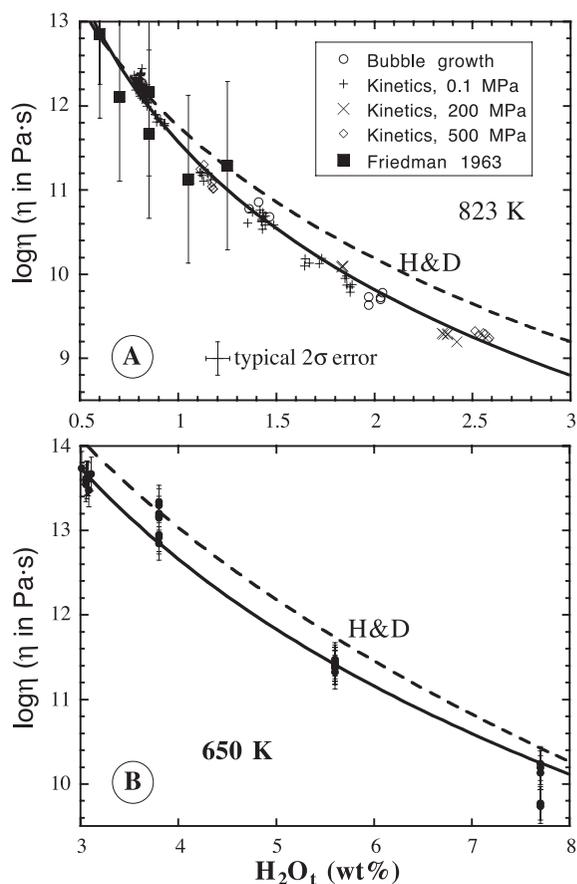
inferred from kinetic experiments and those from bubble-growth experiments lie in the same trend. As can be seen from the scatter of the data around the solid curve (about 0.2 log unit), the  $2\sigma$  uncertainty in the value 11.45 is about 0.2. This uncertainty reflects the real uncertainty in inferring  $\log\eta$  (mostly due to the  $T_{ae}$  estimation using Eq. 3). This constant of  $11.45 \pm 0.2$  is in excellent agreement with the value (11.5) obtained from heat-capacity studies on haplogranitic compositions (Toplis et al. 2001). Sipp and Richet (2002) investigated the constant relating high-precision DTA measurements and viscosity for a wide range of compositions (e.g.,  $\text{SiO}_2$  from 0 to 80 wt%). Their high-precision data show that the “constant” does truly vary (instead of random uncertainty) with composition by about 0.22 ( $2\sigma$  variation)  $\log\eta$  units. For the present study, the compositional range is smaller and the variation in the constant is expected to be smaller than 0.22 and is within the scatter of viscosity inference.

Figure 2a also shows that there is general agreement between our data and those of Friedman et al. (1963), although the scatter in data of Friedman et al. (1963) is large (Friedman et al. stated that uncertainty in viscosity is one log unit). In addition, Figure 2a examines the pressure effect on viscosity (e.g., Bottinga and Richet 1995). It shows that the pressure effect is within experimental uncertainty (0.2 log units) for pressures  $\leq 500$  MPa. Because the pressure effect is small in this pressure range, and we need a large database to investigate the dependence of viscosity on temperature and  $\text{H}_2\text{O}_t$  content, we ignored the pressure dependence and used all viscosity data at  $P \leq 500$  MPa in our effort to model viscosity.

#### Advantages and disadvantages of the experimental technique

There are some advantages in extracting viscosity of hydrous silicate melt from controlled cooling-rate experiments, including:

(1) The main advantage is that problems associated with dehydration and bubble growth during the experiment can be



**FIGURE 2.** Comparison of viscosity data. (a) Data from various sources in the  $\text{H}_2\text{O}_t$  range of 0.5 to 3.0 wt% and in the temperature range of 723–923 K adjusted to 823 K using Equation 6. There is no discernible pressure effect within the uncertainty of the data. (b) Data in the  $\text{H}_2\text{O}_t$  range of 3.0 to 8.0 wt% and in the temperature range of 600–700 K adjusted to 650 K. The dashed curve is calculated from the model of Hess and Dingwell (1996). The solid curve is a fit by Equation 8. The  $2\sigma$  uncertainty is 0.15 to 0.3 log units for viscosity data from bubble-growth experiments (Table 3), 0.25 log units for data from kinetic experiments (Table 2), and 1 log unit for data from compaction experiments (Friedman et al. 1963). Note that the concentration unit here is wt%, whereas that in Equations 8 and 10 is mole fraction.

avoided easily by carrying out the experiments at a pressure greater than the saturation pressure. Hence, viscosity can be obtained for melts with high  $\text{H}_2\text{O}_t$  (such as 8 wt%).

(2) The method can be extended to high pressures to evaluate the effect of pressure on viscosity. Viscosity determination of hydrous melts at high pressures and high viscosities has always been difficult using other methods (e.g., Schulze et al. 1999). As long as the equilibrium constant as a function of temperature is known at high pressure, there is no additional experimental difficulty (i.e., no need to develop new apparatus or method).

(3) The same experimental data can be used both to infer the viscosity of hydrous melts and to calibrate the hydrous species geospeedometer (Zhang et al. 1997b, 2000).

(4) Because the viscosity and geospeedometer calibrations

are related, it might prove more accurate to calibrate the geospeedometer using the vast amount of viscosity data if all viscosity data can be brought into consistency.

Disadvantages of the technique include:

(1) The viscosity of dry melt and melt with less than 0.5 wt%  $H_2O_t$  cannot be determined by this technique because  $H_2O_m$  is low and cannot be measured well. Fortunately, micro-penetration and parallel plate methods are expected to work well for these  $H_2O_t$  contents. Hence, the different methods are complementary.

(2) To determine viscosity using the proposed method, it is necessary to calibrate the dependence of  $K$  on temperature (and pressure if viscosity is to be determined at high pressures), melt composition, and  $H_2O$  content, which is much hard work. Currently, among natural melts, the speciation has been studied only for high- $SiO_2$  rhyolitic melt (MCR in Table 1), allowing easy application of the technique. [Preliminary investigations of speciation have been carried out for a few synthetic systems reviewed in Behrens and Nowak (2003).] For other natural melts (such as dacitic and andesitic melts), viscosity determination requires a long preparation time. Nevertheless, calibration of the IR method is independently useful for measuring  $H_2O_t$  and species concentrations. The speciation data are independently useful in understanding thermodynamic properties of hydrous silicate melts, H isotopic fractionation between the melt and the vapor phase, and the solubility and diffusivity of  $H_2O$  in melt (Zhang 1999b). Hence the preparations are not solely for viscosity determinations.

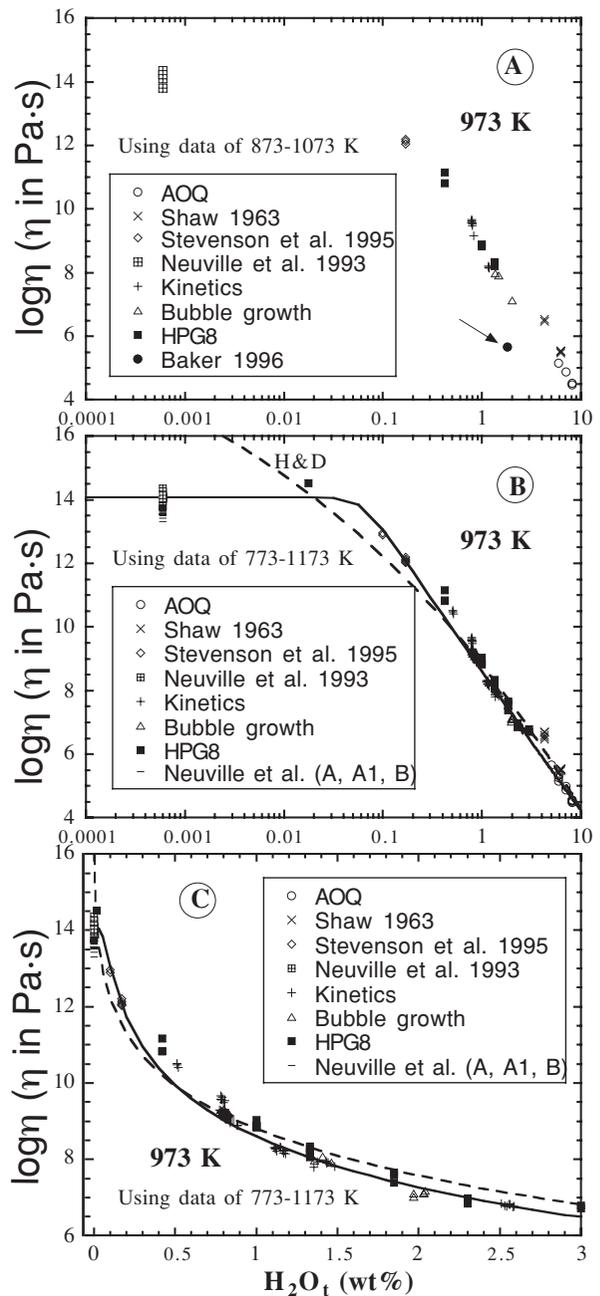
(3) The uncertainty in inferring  $\log \eta$  is large, mainly due to the uncertainty in estimating  $T_{ac}$  (uncertainty in  $q$  is typically negligible), which translates to a  $2\sigma$  uncertainty of about 0.25 in terms of  $\log \eta$ . To improve the precision, better calibration of the relation between species concentrations and temperature (Eq. 3) is necessary.

In conclusion, our method is a useful alternative for obtaining viscosity of hydrous rhyolitic melts at high  $H_2O_t$  contents and high pressures. It is complementary to other methods, although direct methods for viscosity determination, if available, are preferable due to their high precision and model independence.

### The dependence of viscosity on $H_2O$ content

Figure 2 shows viscosity data obtained from bubble growth (Liu and Zhang 2000), kinetic (Zhang et al. 1997b, 2000), and compaction (Friedman 1963) experiments. In addition to general consistency among the data, Figure 2a shows that at 823 K, when  $H_2O_t$  increases from 0.5 to 2.5 wt%, the viscosity decreases by about 4 orders of magnitude.

To examine the dependence of viscosity on  $H_2O_t$  over a wider  $H_2O$  range, data covering a large temperature interval must be used and corrected to a single temperature. As viscosity data on hydrous rhyolitic melt are limited, we also included data on AOQ and HPG8 melts. (Note that viscosity data for HPG8 melt are used to help define the general trend so that we can choose a function for the viscosity dependence on  $H_2O_t$ , but not in our quantitative model because there is a small systematic difference between viscosity of HPG8 and MCR melts.) Figure 3a shows viscosity data in the temperature range of 873–1073 K



**FIGURE 3.** Dependence of viscosity of hydrous rhyolitic melts (MCR, Rhyolite1, Rhyolite3, EDF, BL6, AOQ and HPG8) on  $H_2O_t$  content at 973 K. (a) Using data of 873–1073 K adjusted to 973 K (Eq. 6). The arrow points to the datum of Baker (1996). (b) Using data of 773–1173 K adjusted to 973 K. (c) Similar data as **b** but the horizontal axis is linear. Data uncertainty ranges from 0.1 to 0.3 in  $\log \eta$  (not shown so that the symbols can be seen). Data for samples A, A1 and B from Neuville et al. (1993) are shown in (b) but not used in developing our model. The solid curve in (b) is a fit of the viscosity data (Eqs. 8 or 10). The dashed curve marked H&D is calculated from the model of Hess and Dingwell (1996). Note that the concentration unit here is wt%, whereas that in Equations 8 and 10 is mole fraction.

adjusted to 973 K. Although the general trend is there (and the datum of Baker 1996 marked by the arrow can be seen to be off the trend), there are no data in the  $H_2O_i$  range of 10 ppm to 0.17 wt%. To define the trend better, Figure 3b includes data in the temperature range of 773–1173 K, again adjusted to 973 K.

For most samples, adjustment to the single temperature 973 K is made using Equation 6. Samples with 6 ppm  $H_2O_i$  (Neuville et al. 1993) must be dealt with differently because: (1) the H&D model was not calibrated at such low  $H_2O_i$  and hence cannot be used to predict viscosity; and (2) there are systematic differences in low-temperature viscosity measurements among different sets of samples (A, A1, B, B1, and D) studied by Neuville et al. (1993). On average, viscosities measured on sample A are smaller than those on samples A1 and B by 0.3 log units, and smaller than those on samples B1 and D by 0.6 log units (Fig. 3b). We choose the data on samples B1 and D (highest viscosity at a given  $T$ ), so that the data are more consistent with other viscosity data at low  $H_2O_i$ . Choosing samples B1 and D also reduces the difference between the H&D model and measured viscosity data. Hence, we fit the viscosity data of sample B1 and D as well as the high temperature viscosity data in Neuville et al. (1993) and obtain the following expression for the viscosity of this dry rhyolitic melt:

$$\eta_1 = \exp(-18.5611 + 49584/T) \quad (7)$$

which is used to adjust viscosity data for samples with 6 ppm  $H_2O_i$  to 973K.

From Figure 3, at  $H_2O_i > 0.1$  wt%,  $\log \eta$  is roughly linear to  $\log(H_2O_i)$  and viscosity varies by 9 orders of magnitude, from  $10^{13}$  Pa·s at 0.1 wt%  $H_2O_i$  to about  $10^4$  Pa·s at 10 wt%  $H_2O_i$ . At  $H_2O_i$  range of 0.01 to 0.1 wt%, this power relation does not hold any more and  $\log \eta$  does not increase rapidly with decreasing  $\log(H_2O_i)$ . Below 0.01 wt%  $H_2O_i$ , viscosity is about  $10^{14}$  Pa·s and does not change much with further decreasing  $H_2O_i$  content. That is, for viscosity measurement at this temperature, a dry melt is a melt with less than 100 ppm (0.01 wt%)  $H_2O_i$ .

### Critique of the Hess and Dingwell (1996) viscosity model

Before 1996, the viscosity model of Shaw (1972) was the only one available for estimating hydrous melt viscosity. After extensive experimental work by many groups, H&D developed a much improved viscosity model (Eq. 5) for hydrous rhyolitic melt applicable to both high and low temperatures. Although the model achieved great success, there is still room for improvement along the following lines:

(1) Large uncertainty. As stated by Hess and Dingwell (1996), the  $2\sigma$  uncertainty in the H&D model is still high, 0.92 in terms of  $\log \eta$  (a factor of 8 in terms of  $\eta$ ).

(2) Small systematic error. Figures 2 and 3 show that the H&D model (dashed curve) is not much off from the data, but there is a resolvable small systematic error in the model, as pointed out by Liu and Zhang (2000). From Figures 2a and 2b, the small systematic error reaches a maximum at 2–4 wt%  $H_2O_i$ .

(3) Large error for dry rhyolitic melt (such as 6 ppm  $H_2O_i$ ). This can be seen in Figure 3b where the dashed curve misses the data at 6 ppm  $H_2O_i$  by a couple orders of magnitude. The empirical relation between  $\log \eta$  and  $\ln(w)$  in the H&D model

that characterizes the dependence of viscosity on  $H_2O_i$  is theoretically unappealing because Equation 5 cannot be extended to dry melt: as total  $H_2O$  content decreases to zero, the viscosity would first increase, and then decrease to zero. As seen in Figure 3b, this inability to handle viscosity of melts with very low  $H_2O_i$  content begins to become significant at  $\leq 0.2$  wt%  $H_2O_i$ . For example, at  $H_2O_i = 0.1$  wt%, experimental viscosity data is about 5 times the calculated viscosity using H&D model. Hence, we need a new mixing law for the viscosity of  $H_2O$ -rhyolite system that is at least theoretically extendible to dry melts.

Possible explanations for the first two problems cited above in the H&D viscosity model are as follows:

(1) H&D used viscosity data with various melt compositions to develop their viscosity model (see Table 1). These melts with different anhydrous compositions might have different viscosities at the same  $T$  and  $w$ , hence causing the large uncertainty of the model (see later discussion).

(2) H&D used some data with relatively large uncertainties, such as the data of Baker (1996) and Friedman et al. (1963). The viscosity datum of Baker (1996) (see filled circle with an arrow in Fig. 3a) is clearly an outlier (off by about a factor of 100 compared to other data), and the data of Friedman et al. have a stated uncertainty of one log unit (Fig. 2) whereas most other viscosity data have a stated uncertainty of about 0.1 log units. Because H&D did not weight the data by the uncertainty in their nonlinear fit, any measurement with a large uncertainty might have had an unwittingly large effect on their model.

(3) In the calibration of the model by H&D, the constraints in the viscosity range of  $10^9$ – $10^{12}$  Pa·s are mostly from micropenetration measurements on hydrous HPG8 melt (Dingwell et al. 1996). First, the composition of HPG8 is slightly different from that of MCR (see Table 1 for compositions), and its viscosity appears to be slightly higher (see later). Hence, lumping HPG8 with other rhyolites to model viscosity may produce a small systematic difference. Secondly, dehydration during micropenetration determination for viscosity of hydrous melt might have affected the value of the measured viscosity, although the magnitude of the problem cannot be quantified.

Because of these considerations, we develop a new viscosity model based on our new data as well as data from the literature. First, we propose a mixing “law” for the viscosity of hydrous silicate melt to model the dependence of viscosity on  $H_2O_i$ . Then we construct a model for the viscosity as a function of temperature and  $H_2O_i$  for a rhyolitic melt with a narrow range of anhydrous compositions.

### Modeling the dependence of viscosity on $H_2O$ content

We tried many different ways to fit the viscosity data in Figure 3. The following equation fit the data almost perfectly:

$$\frac{1}{\eta} = \frac{1}{\eta_1} + \left(\frac{1}{\eta_2} - \frac{1}{\eta_1}\right)x^n \approx \frac{1}{\eta_1} + \frac{1}{\eta_2}x^n \quad (8)$$

where  $1/\eta$  is fluidity,  $\eta_1$  is the viscosity of the dry melt (a function of  $T$  and anhydrous composition),  $x$  is  $H_2O_i$  content (such as mole fraction on a single oxygen basis),  $n$  and  $\eta_2$  are two fitting parameters (both are functions of  $T$ ), and  $\eta_2$  can be iden-

tified to be the viscosity of the hypothetical melt made of pure  $H_2O$  ( $\eta_2$  cannot be measured directly because such a melt does not exist). An excellent fit to the viscosity data in Figure 3b by Equation 8 is shown as the solid curve (note that although the horizontal axis is in wt%, the fit is done using Eq. 8 with mole fractions of  $H_2O_i$ ). Hence, we propose this relation as the mixing "law" for modeling viscosity of hydrous melts.

Figure 3 shows that viscosity of AOQ melt (open circles) is similar to rhyolitic melt viscosity but that of HPG8 melt (solid squares) is slightly greater than that of rhyolitic melt. Using Equation 8, the addition of the first 1 wt%  $H_2O_i$  decreases the melt viscosity slightly more than the addition of another 9 wt%  $H_2O_i$ . At 973 K, the viscosity of a melt containing 0.1 wt%  $H_2O_i$  is less than that of a "dry" melt (less than 100 ppm  $H_2O_i$ ) by 1.2 orders of magnitude (Fig. 3). At higher temperatures, the effect of  $H_2O$  on viscosity is smaller.

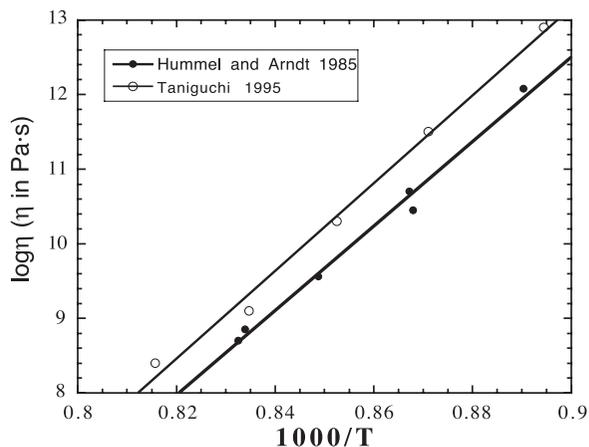
Figure 3 also shows the need to obtain viscosity data for rhyolitic melts with 10 to 1000 ppm  $H_2O_i$ . Such data would either verify our proposed mixing law for viscosity of hydrous melts (Eq. 8) or point out the need to modify it.

Some authors often report viscosity of "dry" melts without reporting the  $H_2O$  concentration. Such a practice should be discontinued. (Another practice, reporting the nominal melt composition such as albite, but without accompanying microprobe analysis, should also be discontinued.) Because such a melt may still contain some  $H_2O_i$ , such as several hundred ppm, it is possible that the minute  $H_2O_i$  still affects the melt viscosity significantly, especially at low temperatures (i.e., high viscosity). Due to the strong dependence of viscosity on dissolved  $H_2O_i$ , viscosity data for "dry" melt without reporting the  $H_2O_i$  must be treated with caution. Some scatter in viscosity data in the literature, such as the viscosity of anorthite melt (Fig. 4) and of albite melt (Hummel and Arndt 1985; Romano et al. 2001), might be due to slightly different  $H_2O_i$ . (It might also be due to differences in the anhydrous composition, Toplis et al., 1997.) With infrared spectroscopy, measurement of  $H_2O_i$  at low  $H_2O_i$  is not particularly difficult, except for calibration. The molar absorptivity of the  $3500\text{ cm}^{-1}$  band varies between 8.0 and  $6.0\text{ L/mol}\cdot\text{mm}$  for rhyolitic to basaltic glass (Ihinger et al. 1994; Mandeville et al., 2002). Hence, we suggest reporting a rough estimate of  $H_2O_i$  (as well as the IR band intensity) by estimating the molar absorptivity for the appropriate composition. It is better to know  $H_2O_i$  to within 30% relative, or an upper limit of  $H_2O_i$ , than not knowing it at all.

#### A model for viscosity of hydrous rhyolitic melt

In this section, we develop a new viscosity model for hydrous rhyolitic melt on how the viscosity depends on both temperature and  $H_2O_i$ . Our goal is limited and is similar to that of H&D: to develop a viscosity model for hydrous melt with a "single" dry melt composition. Development of a comprehensive viscosity model applicable to a range of silicate melt compositions is a much more daunting task that will have to await future work.

One step we take to improve input data consistency is to restrict the melt composition. It is expected that viscosity depends on anhydrous melt composition. Hence, restricting our study to a narrower compositional range is necessary to model melt viscosity more accurately. The effect of anhydrous melt



**FIGURE 4.** Viscosity of anorthite melt. The results of Hummel and Arndt (1985) are systematically lower by about 0.56 log units. This systematic difference might be attributed to a small difference in  $H_2O$  content, such as 500 ppm vs. 200 ppm. It might also be due to compositional difference (Taniguchi 1995 did not report the chemical composition).

composition must be addressed separately.

Characterizing the compositional differences among multi-component melts is not straightforward. Instead of finding the compositional difference in terms of distance in a multicomponent composition space, it is easiest to use one single compositional parameter. Unfortunately, for complicated rhyolitic and granitic melts, no one parameter has been found yet that can quantitatively describe how the melt viscosity depends on composition. One simple measure is the total concentration of network formers ( $SiO_2 + Al_2O_3$ ). We list the sum of cation mole fraction of Si and Al associated with Na and K (in the form of  $NaAlO_2$  and  $KAlO_2$ ), called  $Si + Al^T$ , in Table 1. This simple parameter is not intended to capture all the variation of viscosity with composition, but to indicate the similarity of different melts for a small compositional range shown in Table 1. As shown in Table 1, there is a cluster of rhyolites with  $Si + Al^T = 0.847$ . Hence we decided to construct a viscosity model for rhyolitic and haplorhyolitic melts with  $Si + Al^T = 0.847 \pm 0.007$ .

Using this compositional range, the following viscosity data have been used in constructing our new viscosity model: data on MCR (Tables 2 and 3), AOQ (Schulze et al. 1996), Rhyolite1 (Shaw 1963), and Rhyolite3 (Friedman et al. 1963). We also included the following data that were not used by H&D: BL6 and EDF (Stevenson et al. 1995) (LGB-1 in the same paper was not included because its  $H_2O_i$  content was not reported), and samples B1 and D for Rhyolite2 (Neuville et al. 1993). The following data that were used by H&D were not used in this study:

(1) Viscosities of hydrous HPG8 melt (Hess et al. 1995; Dingwell et al. 1996; Dorfman et al. 1996) were not used because HPG8 has a slightly different composition (Table 1) with  $Si + Al^T = 0.863$ . The viscosity is also slightly different (Fig. 3b); (2) The data of Persikov et al. (1990) (Rhyolite4 in Table 1) and Scailet et al. (1996) (GB4 in Table 1) are for different compositions. These melts have significantly smaller  $Si + Al^T$  than MCR (Table 1). Hence, viscosity data on them were not included in this model; (3) The three data points on Rhyolite5

by Burnham (1964) were published only in an abstract and details are not known. Hence the data were not used; (4) The single viscosity measurement by Baker (1996) is clearly an outlier. As shown in Figure 3a, this single point (filled circle with an arrow) is off from the trend defined by other data by about 2 orders of magnitude. Hence, this datum was not included; (5) The viscosity data on rhyolitic samples A, B, and A1 in Neuville et al. (1993) were not used. These data are different from data on samples D and B1, and we can only choose one set to be self-consistent (see earlier discussion). We chose the set with highest viscosity to be more consistent with other viscosity data at about 0.1 wt% H<sub>2</sub>O<sub>i</sub>.

The selected data cover the temperature range of 570 to 1920 K and H<sub>2</sub>O<sub>i</sub> range of 0.0006 to 8.2 wt%, although the coverage is not uniform (e.g., no data between 0.0007 to 0.02 wt% H<sub>2</sub>O<sub>i</sub>). The data were fit to the specified functions using a weighted nonlinear regression with the Levenberg-Marquardt method (Press et al. 1992). The algorithm seeks values of the fitting parameters that minimize  $\chi^2$ , the sum of the squared weighted differences (the difference between the observed and the predicted  $\log\eta$  divided by the uncertainty). Our algorithm is slightly different from that of H&D, who used an unweighted nonlinear regression. The error assignments are as follows: for viscosity inferred from cooling rate experiments (Table 2),  $2\sigma$  uncertainty in  $\log\eta$  is assigned to be 0.25 to 0.30 depending on the quality of the IR spectrum; for viscosity inferred from bubble-growth experiments,  $2\sigma$  uncertainty in  $\log\eta$  is as given in Table 3; for the high viscosity of Rhyolite2,  $2\sigma$  uncertainty in  $\log\eta$  is chosen to be 0.3 to account partially for the large differences among different samples (A, A1, B, B1, and D); for other viscosity data,  $2\sigma$  uncertainty in  $\log\eta$  is the same as assigned by the original authors but at least 0.1 (to account for other errors such as interlaboratory difference).

Taking the logarithm of both sides of Equation 8, our viscosity model has the following form:

$$\log\eta = -\log\left(\frac{1}{\eta_1} + \left(\frac{1}{\eta_2} - \frac{1}{\eta_1}\right)x^n\right). \quad (9)$$

The above formulation avoids the problem of undefined viscosities for dry melts in the H&D model. The expression of  $\eta_1$  is given in Equation 7. To proceed with fitting using Equation 9, we need an empirical expression for  $\eta_2$ . Either of the following two empirical equations can account for the non-Arrhenian temperature dependence of melt viscosity (e.g., Brush 1962):

$$\log\eta = A + B/(T - T_0) \quad (9a)$$

$$\text{and } \log\eta = a + (b/T)^m. \quad (9b)$$

Both of the above equations are three-parameter equations and they both fit experimental viscosity data well. Equation 9a is the VFT equation. It runs into problems at  $T < T_0$ :  $\eta$  calculated from Equation 9a has no meaning when  $T < T_0$ . For some melts such as anorthite,  $T_0$  is 850 K, and calculated viscosity would be undefined for a large temperature range (0–850 K). Hence, we opt for Equation 9b to account for the non-Arrhenian temperature dependence of viscosity.

Preliminary trial fits show that the parameter  $n$  in Equation

9 depends on temperature. After numerous trials of weighted nonlinear regressions with different functions, the data were fit by the following six-parameter equation:

$$\log\eta = -\log\{\exp(18.5611 - 49584/T) + \exp[1.47517 - (1795.5/T)^{1.9448}]x^{1 + (1812.2/T)^2}\}. \quad (10)$$

In the above equation,  $\eta_1$  is from Equation 7, and the form of  $\eta_2$  is from Equation 9b. The above formula reproduces the viscosity data with a standard deviation ( $2\sigma$ ) of 0.36 in terms of  $\log\eta$  (except for data of Friedman et al. 1963 as those data have much larger uncertainties).

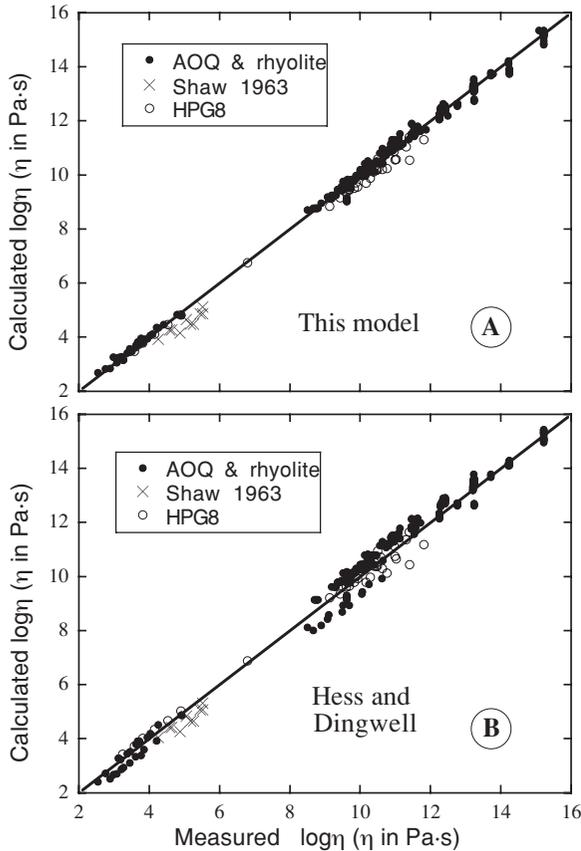
As shown in Figure 3,  $\log\eta$  for our model at low H<sub>2</sub>O concentration is pinned by the data of Neuville et al. (1993). Figure 3b shows that on a  $\log\eta$  vs.  $\log(\text{H}_2\text{O}_i)$  plot, our model produces a bend at about 600 ppm H<sub>2</sub>O<sub>i</sub>. To examine whether the bend is an artifact of the choice of axes, the same data are shown in Figure 3c but with a linear H<sub>2</sub>O<sub>i</sub> horizontal axis. The figure shows that as H<sub>2</sub>O<sub>i</sub> decreases toward zero, although  $\log\eta$  increases monotonically, the rate of  $\log\eta$  increase is not monotonic, with a bend at 600 ppm. If the melt viscosity at 6 ppm H<sub>2</sub>O<sub>i</sub> was greater than that determined by Neuville et al. (1993), Equation 9 would still be able to fit the data well, and the non-monotonic rate of  $\log\eta$  increase as H<sub>2</sub>O<sub>i</sub> decreases toward zero would still be present although the bend would occur at an even lower H<sub>2</sub>O<sub>i</sub>. The non-monotonic nature for the rate of  $\log\eta$  change is counter-intuitive, suggesting that there is a need to further improve the functional form of Equation 9.

#### Comparison of our new viscosity model with the model of Hess and Dingwell (1996)

As argued by H&D, their model is the best one available for viscosity of hydrous rhyolitic melt. Hence, here we compare our new model with their model only. Both the H&D model and our model involve six parameters. The  $2\sigma$  uncertainty is 0.92 log units for the H&D model and 0.36 for our model. Figure 5 shows that our model predicts viscosity values with a smaller uncertainty than the H&D model.

However, the simple comparison by  $2\sigma$  reproducibility or in Figure 5 is not entirely fair as some of the improvement of our model over the H&D model is due to our stricter choice of the rhyolitic melt composition as well as the exclusion of an outlier. We hence show the comparison of various data in Table 4. For a given set of viscosity data with a fixed or a narrow range of anhydrous melt composition, we calculate  $\Delta \pm 2\sigma$ , where  $\Delta$  is the average difference between the experimental  $\log\eta$  and model calculated  $\log\eta$ , and  $\sigma$  is the standard deviation. That is, the value of  $\Delta$  represents systematic difference in viscosity and  $2\sigma$  is a measure of data scatter (and model scatter). The  $2\sigma$  range of departure of experimental data from model is  $\Delta - 2\sigma$  to  $\Delta + 2\sigma$ . For example, if a melt has a lower viscosity compared to MCR,  $\Delta$  would be negative. If  $\Delta$  is roughly zero, then there is no systematic difference. Table 4 shows the following statements. (1) For MCR, Rhyolite1, EDF, BL6, and AOQ melts,  $\Delta \sim 0$  for both models, but the  $2\sigma$  scatter of our model (0.37 log units) is smaller than the H&D model (0.62 log units). (2) For the data of Friedman et al. (with a  $2\sigma$  uncertainty of 1 log unit according to the original authors), our model

does not reproduce the data as well as the H&D model. This result is because we used a weighted nonlinear regression that de-emphasized the data of Friedman et al. (1963). This is the only data set that the H&D model does better than our model. (3) For Rhyolite2 with 6 ppm  $H_2O_i$  (sample D and B1 of



**FIGURE 5.** Comparison of measured viscosity data of rhyolitic melts (MCR, AOQ, EDF, BL6, and Rhyolite1) with (a) those calculated from Equation 10 of this work; (b) those calculated from the model of Hess and Dingwell (1996). Data on Rhyolite2 are included in a but not in b because H&D did not use the data in their model and including the data would make b a mess. Data on Rhyolite3 are not shown because the stated uncertainties are large. The solid line in both diagrams is a 1:1 line. Data on HPG8 (Dingwell et al. 1996) are used by the model of Hess and Dingwell (1996) but are not in the calibration of our model. Uncertainty of data is mostly 0.1 to 0.3 log units and they are not shown to make the symbols in the figures more readable.

Neuville et al. 1993), our model reproduces the data with no systematic error and with a  $2\sigma$  of only 0.19 log units, but the H&D model has a systematic error of 2 log units plus an additional scatter of 1 log unit. This result is because we used the data in our model but H&D did not use the data. It also shows that the H&D model cannot be extended to dry melts. (4) For viscosity data of HPG8 melt that were used by H&D but not by us in constraining the model, our model systematically underestimates its viscosity by 0.24 log units with a scatter of 0.41 log units, whereas the H&D model shows no systematic difference but with a scatter of 0.61 log units. The range of deviation ( $\Delta - 2\sigma$  to  $\Delta + 2\sigma$ ) using our model to predict the viscosity of HPG8 is  $-0.17$  to  $0.64$  log units, whereas the range of deviation using the H&D model is  $-0.59$  to  $0.63$  log units. That is, for this melt, our model predicts its viscosity slightly better than the H&D model, which can also be seen from Figure 5, even though we did not use the data to constrain our model. Furthermore, our model reveals that viscosity of HPG8 melt is higher than that for AOQ and MCR, which is consistent with Figure 3 and the fact that  $Si + Al^T$  for HPG8 is slightly greater. Therefore, if we add 0.24 to  $\log \eta$  calculated from Equation 10, we can predict viscosity of HPG8 to within 0.41 log units, about the same accuracy as that for MCR and AOQ melts. This example confirms that our narrowing the anhydrous melt composition is in the right direction to improve viscosity models. (5) For data on GB4 and Rhyolite4, which were used by H&D but not by our model, both models predict the viscosity to about the same accuracy. Furthermore, there is systematic difference in viscosity between these melts and MCR/AOQ.

Table 4 also shows that, when the low-quality data of Friedman et al. (1963) are not considered, viscosity for rhyolitic melts listed in Table 1 increases as  $Si + Al^T$  increases (Fig. 6), consistent with expectations.

In summary, for Mono Crater rhyolite and other melts with similar composition (AOQ, Rhyolite1, Rhyolite2, BL6, and EDF), our model predicts viscosity with better accuracy than the H&D model; for all other melt compositions covered by H&D but not by us, our model predicts viscosity to at least the same or better accuracy. Furthermore, as shown in Figures 2 and 3, for the H&D model, there is large systematic error at very low  $H_2O_i$  ( $< 0.2$  wt%), and small systematic error at higher  $H_2O_i$  (1 to 5 wt%). Hence, we recommend our model for calculation of viscosity of high-silica ( $\sim 77$  wt%) rhyolitic melt, as well as other metaluminous leucogranite or calc-alkaline rhyolitic melts. Because the viscosity data used to calibrate our model span essentially the whole  $T - H_2O_i$  range (570–1920 K, 6 ppm to 8.2 wt%  $H_2O_i$ ) of rhyolitic melts in silicic volcanism,

**TABLE 4.** Comparison of fits of data by our viscosity model and H&D model

Sample	$Si + Al^T$	$\Delta \pm 2\sigma$ in reproducing $\log \eta$ This model	$\Delta \pm 2\sigma$ in reproducing $\log \eta$ H&D model
a. MCR, Rhyolite1, EDF, BL6, AOQ	0.847	$0.02 \pm 0.37$	$-0.09 \pm 0.62$
b. Rhyolite2 (samples D and B1)	0.854	$0.00 \pm 0.19$	$-2.19 \pm 1.10$
c. Rhyolite3 (Friedman 1963)	0.848	$-0.15 \pm 1.31$	$0.02 \pm 1.14$
d. HPG8, dry and hydrous ( $N = 33$ )	0.863	$0.24 \pm 0.41$	$0.02 \pm 0.61$
e. GB4 ( $N = 11$ )	0.814	$-0.16 \pm 0.32$	$-0.23 \pm 0.34$
f. Rhyolite4 ( $N = 9$ )	0.807	$-0.56 \pm 0.87$	$-0.58 \pm 0.98$

*Notes:*  $\Delta$  is the average value of  $\log \eta_{\text{exp}} - \log \eta_{\text{calc}}$ , and  $2\sigma$  is two times the standard deviation of  $\log \eta_{\text{exp}} - \log \eta_{\text{calc}}$ . Source of viscosity data are listed in footnotes of Table 1.  $N$  in parentheses is the number of data points.

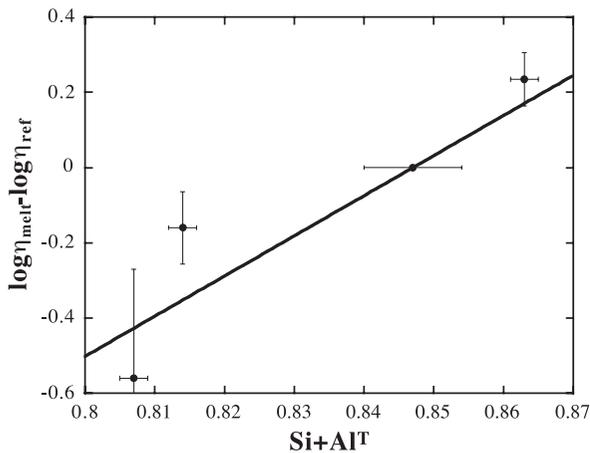


FIGURE 6. Dependence of rhyolite melt viscosity on the parameter  $\text{Si}+\text{Al}^{\text{T}}$ . The straight line is a simple linear fit (not intended for quantitative use).

our model can be applied without extrapolation to calculate viscosity for various magmatic and volcanic processes. Furthermore, better predictions of  $\log \eta$  can be achieved for three specific melts (HPG8, GB4, and Rhyolite4) listed in Table 4, by adding a constant  $\Delta$  (boldface in Table 4) to the calculated viscosity using Equation 10.

Nevertheless, the uncertainty of our model is still greater than the reported uncertainty of experimental viscosity data (typically 0.06 log unit). Relative to the reported uncertainty, the following data are not well fit by Equation 10: (1) The data of Shaw (1963) at 4.3 wt%  $\text{H}_2\text{O}$ ; (2) the data of Friedman et al. (1963) at  $\text{H}_2\text{O}_i \leq 0.15$  wt%; and (3) some of the viscosity data inferred from kinetic experiments (Table 2). Because the kinetic data set is highly self-consistent and can be well fit as a geospeedometer ( $2\sigma$  uncertainty in  $\log \eta$  being 0.17; Zhang et al. 2000), the large misfit with the viscosity model is attributed to one or more of the following: (1) imperfect model for  $T_{\text{ae}}$  calculation (Ihinger et al. 1999); (2) imperfect calibration of the IR technique for  $\text{H}_2\text{O}_i$  determination (Zhang et al. 1997a); and (3) imperfect Equation 9 (that is, more terms involving  $x$  may be necessary). To further improve the viscosity model, it is necessary to: (1) improve the various calibrations; (2) critically assess all viscosity data to bring them into consistency; and/or (3) develop a better relation between viscosity and  $\text{H}_2\text{O}_i$  than that of Equation 9, e.g., by adding more terms to Equation 9.

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