

Granitic melt viscosities: Empirical and configurational entropy models for their calculation

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ABSTRACT

Newly measured viscosities of a low H₂O-content granitic melt and a low H₂O-content albitic melt have been combined with viscosity data from the literature to create two new models for the calculation of granitic melt viscosities at crustal pressures and temperatures between 700 and 900 °C; one model is purely empirical, and the other is based on configurational entropy theory. When the molecular weight of the anhydrous melt is calculated on the basis of eight O atoms, or assumed to be 260 gram formula weight (gfw), and the total H₂O concentration is expressed by its mole fraction, the viscosity, η , of per- and metaluminous granitic melts, ~70–76 wt% SiO₂, can be calculated from the following empirical equations: For $X_{\text{H}_2\text{O}}^{\text{tot}} \leq 0.25$,

$$\log \eta = (0.0292649T - 53.198903)X_{\text{H}_2\text{O}}^{\text{tot}} - 0.0129207T + 24.2973$$

and for $X_{\text{H}_2\text{O}}^{\text{tot}} > 0.25$,

$$\log \eta = -2.2977826X_{\text{H}_2\text{O}}^{\text{tot}} - 0.0095110T + 15.6293$$

where viscosity is in pascal-seconds, and temperature, T , is in kelvins. The first equation expresses the effects of H₂O addition on melt viscosity at low H₂O contents where the predominant H₂O species in the melt is OH⁻ (as demonstrated in previous studies) and small additions of H₂O have large effects on melt viscosity; above $X_{\text{H}_2\text{O}}^{\text{tot}} \approx 0.25$, molecular H₂O is the dominant species of H₂O, the addition of which has only modest effects on melt viscosities. This empirical model is applicable to granitic melts with total H₂O contents between 0.3 and 12.3 wt%. Following configurational entropy theory, viscosities of the same hydrous granitic melts can be calculated by modeling the viscosities as ternary mixtures of various mole fractions of molecular H₂O, $X_{\text{H}_2\text{O}}$, OH⁻, X_{OH^-} , and silicate melt, $X_{\text{silicate melt}}$: $\ln \eta = -15.398 + [181.622/\{T[S_{\text{conf}}(X_{\text{silicate melt}}) - R(C_{\text{H}_2\text{O}}X_{\text{H}_2\text{O}} \ln X_{\text{H}_2\text{O}} + C_{\text{OH}^-}X_{\text{OH}^-} \ln X_{\text{OH}^-} + C_{\text{silicate melt}}X_{\text{silicate melt}} \ln X_{\text{silicate melt}})\}]$, where S_{conf} , the configurational entropy calculated from the viscosity measurements, is 4.567×10^{-3} J/(mol·K); R is the gas constant, 8.314 J/(mol·K); $C_{\text{H}_2\text{O}}$ is -1.899×10^{-3} ; C_{OH^-} is -1.531×10^{-3} ; and $C_{\text{silicate melt}}$ is 4.913×10^{-3} . Mole fractions of H₂O and OH⁻ are estimated from previously published measurements of species abundances in quenched rhyolitic glasses, and the molecular weight of the silicate melt is 260 gfw. Application of this model is limited to melts with a maximum of approximately 6 wt% total H₂O because $X_{\text{H}_2\text{O}}-X_{\text{OH}^-}$ speciation information is not available at higher H₂O contents. Numerical values in the above equation are not considered to have any physical or chemical significance. Calculated granitic melt viscosities deviate on average from measured viscosities by -0.03 log units for the empirical model and -0.2 log units for the configurational entropy model. At H₂O concentrations below 4 wt% and above 7 wt%, these models for viscosity estimation are significantly better than previous models, which can be in error by one to two orders of magnitude. Using either of these new models, the viscosities of granitic melts with 1–3 wt% H₂O are calculated to be up to two orders of magnitude lower than previously thought. This results in a one to two order-of-magnitude increase in the viscosities of melt extraction from source regions, transport of melts through the crust, and Stokes settling of crystals.

INTRODUCTION

Recent experiments investigating the dehydration melting of common crustal lithologies have demonstrated

that such bulk compositions produce near-solidus partial melts similar in composition to granitic rocks at lower crustal pressures and temperatures between 700 and 950 °C (e.g., Rutter and Wyllie 1988; Vielzeuf and Holloway

1988; Vielzeuf et al. 1990; Patiño Douce and Johnston 1991; Skjerlie and Johnston 1992). Because of the low H₂O content of the source rocks undergoing anatexis, granitic melts produced at 30–60% melting are likely to contain approximately 2–3 wt% dissolved H₂O. Such relatively low H₂O concentrations in melts are consistent with comparisons of the phase equilibria of natural granites with their petrography (Maaloe and Wyllie 1975; Clemens et al. 1986). Further evidence for the existence of low H₂O-content granitic melts is based on direct H₂O concentration measurements and thermodynamic calculations of dissolved H₂O by Clemens (1984); he demonstrated that many intermediate to silicic magmas had H₂O contents significantly below 4 wt%. Despite the apparent abundance of these “damp” granitic magmas, we have little knowledge of the physical properties of low H₂O-content granitic melts. Viscosity is one such important physical property that affects the rates at which granitic melts separate from their source rocks, accumulate into dikes or diapirs, and ascend into the upper crust where they may cool and form plutons or become magma chambers for rhyolitic volcanoes. Viscosities used to calculate melt-transport rates frequently are estimated by the method of Shaw (1972), which was based on experiments with less than 0.65 wt% H₂O and with 4.5 and 6.2 wt% H₂O. Very few viscosity data exist for granitic melts with H₂O concentrations in the estimated range of many natural granitic magmas. The few data that do exist demonstrate that the method of Shaw (1972) overestimates viscosities of granitic melts containing between 1 and 3.5 wt% H₂O by one to two orders of magnitude. These differences between measured and calculated viscosities of low H₂O-content granitic melts result in orders of magnitude differences in melt-transport rates. Such overestimates of low H₂O-content granitic melt viscosities calculated by Shaw’s (1972) method led McKenzie (1985) to conclude that such magmas could not separate from their source regions by simple compaction. This paper presents new models for the calculation of per- and metaluminous granitic melt viscosities at crustal pressures, which accurately reproduce measured viscosities of hydrous granitic melts, including those with only a few weight-percent total H₂O. One model is totally empirical and the other is based on configurational entropy theory. The models are calibrated with viscosity data from the literature and with new viscosity measurements at temperatures of 800 and 1400 °C; they are tested by comparison of calculated and measured granitic viscosities at 700 and 900 °C. Both new models are consistent with our current knowledge of H₂O speciation in silicate melts at high temperatures and pressures (Stolper 1982; Silver et al. 1990) and with one current model of the mechanisms of H₂O dissolution into albite melts (Sykes and Kubicki 1993). The empirical model calculates accurate viscosities at temperatures between 700 and 900 °C for granitic melts containing between 0.3 and 12.3 wt% H₂O, and the configurational entropy model is accurate for the same temperature region and melts with 0.5–6 wt% H₂O.

TABLE 1. Compositions of granitic melts used to construct and test viscosity models

Oxide	Shaw (1963)	Burnham (1964)*	Persikov (1991)	LCO (this study)
SiO ₂	76.6	73.79	73.23	76.37
TiO ₂	0.10	0.05	0.19	0.11
Al ₂ O ₃	12.7	15.11	13.60	13.35
Fe ₂ O ₃	0.58	0.26	2.56	n.a.
FeO	0.56	0.16	0.48	n.a.
FeO _{tot}	n.a.	n.a.	n.a.	0.76
MnO	0.0	0.05	n.a.	0.06
MgO	0.02	0.07	0.17	0.07
CaO	0.31	0.97	1.69	0.51
Na ₂ O	4.1	4.71	3.78	4.31
K ₂ O	4.6	4.02	4.11	4.67
P ₂ O ₅	0.0	0.01	0.13	n.a.
Total	99.57	99.19	99.94	100.21

Note: Friedman et al. (1963) did not provide the composition of the melt studied, but Shaw (1963) considered it compositionally similar to his melt; n.a. = not analyzed.

* Analysis from Burnham and Nekvasil (1986).

EXPERIMENTAL TECHNIQUES AND MEASUREMENTS

Viscosities of an albitic melt, Na_{0.97}Al_{0.99}Si_{3.02}O₈, at anhydrous conditions and with 0.5 wt% H₂O, and a granitic melt, LCO (Table 1), with 1.8 wt% H₂O were determined at high pressures using the falling-sphere technique (Shaw 1963; Scarfe et al. 1987; Baker and Vaillancourt 1995). Glass powders, H₂O (for the hydrous experiments), and platinum spheres were loaded into 3 mm diameter, 3–4 mm long platinum capsules, which were welded closed without volatile loss. To homogenize H₂O along all grain boundaries of the glass powder, these sealed capsules were stored in a 110 °C drying oven for a minimum of 2 h. Capsules were then mounted in the center of 1.91 cm diameter NaCl-Pyrex crushable alumina assemblies (Hudon et al. 1994; Baker and Vaillancourt 1995).

Albite melt viscosities were measured at 1.5 GPa and 1400 °C, and granitic melt viscosities were measured at 1.0 GPa and 800 °C. Pressures were corrected for friction (–12%) on the basis of the melting of NaCl at 1.0 GPa (Bohlen 1984), and pressure is believed accurate to within 25 MPa. Temperature was measured with type-C thermocouples, and experiments were heated at 300 °C/min to within 20 °C of the experimental temperature; the heating rate was then slowed to 50 °C/min until the desired temperature was reached. Temperature was controlled to within ±2 °C, except at the beginning of the experiment when the desired temperature was overshoot by 6–8 °C. Our calibrations of the thermal gradient in our experimental assemblies (Hudon et al. 1994) demonstrate that the entire length of the capsule was within 5 °C of the thermocouple temperature at 800 °C and within 10 °C at 1400 °C. Experiments were quenched at a rate of 2000 °C/min. Experimental capsules were mounted in epoxy, ground open, and polished to measure the distance the platinum sphere sank during the experiment using a microscope with a calibrated reticle.

For each viscosity determination a minimum of two experiments were performed, and viscosities of the falling

TABLE 2. Viscosities of hydrous granitic and albite melts used to construct and test the models

<i>T</i> (°C)	<i>P</i> (MPa)	H ₂ O (wt%)	log η (η in Pa·s)	Reference
Granitic melts				
700	0.1	0.05	11.698	1
700	50	2.1	5.978**	2
700	100	3.3	5.763**	2
700	200	5.2	4.839**	2
700	700	12.3	4.400**	2
700	480–780	8.8	5.110	3
700	200	6.2	5.520	4
735	0.1	0.1	11.818	5
735	0.2	0.15	10.476	5
735	0.3	0.3	10.100	5
735	1.0	0.5	9.476	5
735	2.1	0.65	9.152	5
785	0.2	0.1	10.301	5
785	0.3	0.2	10.100	5
785	1.0	0.5	9.301	5
785	2.1	0.6	8.900	5
800	0.1	0.05	10.500	1
800	1000	1.8	4.411	6
800	50	2.1	5.100	2
800	100	3.3	4.800	2
800	200	5.2	3.970	2
800	700	12.3	3.656**	2
800	200	6.2	4.570	4
800	480–740	8.8	4.144	3
900	0.1	0.05	8.797	1
900	50	2.1	4.377	2
900	100	3.3	3.998	2
900	200	5.2	3.247	2
900	700	12.3	2.800	2
900	480–740	8.8	3.450	3
Albite melts				
1400	1500	0.0	3.030	6
1400	1500	0.5	2.060	6
1400	1500	2.79	1.570	7
1400	1500	5.58	1.370**	8

Note: References are as follows: 1 = Murase and McBirney 1973, 2 = Persikov 1991, 3 = Burnham 1964, 4 = Shaw 1963, 5 = Friedman et al. 1963, 6 = this study, 7 = Dingwell and Mysen 1985, and 8 = Dingwell 1987.

* All values of log η were calculated to three decimal places to minimize rounding errors in calculations.

** Extrapolated from measurements at higher or lower temperatures using Arrhenius equations. In no case was the extrapolation more than 200 °C.

spheres, v , were determined from the slope of lines on plots of distance fallen vs. experimental duration. Glass densities were calculated using the model of Bottinga et al. (1982) or extracted from the literature (Kushiro 1978) and combined with the platinum densities to calculate $\Delta\rho$. This information, together with the radius of the platinum spheres, r , the inner radius of the platinum capsules, r_c , the capsule length, h_c , and Earth's gravitation, g , were used to calculate melt viscosity, η , using Stokes's law with the Faxen correction for wall effects (Shaw 1963; Breatly and Montana 1989; Baker and Vaillancourt 1995):

$$\eta = \frac{2gr^2\Delta\rho}{9v(1 + 3.3r/h_c)} \left[1 - 2.104\left(\frac{r}{r_c}\right) + 2.09\left(\frac{r}{r_c}\right)^3 - 0.95\left(\frac{r}{r_c}\right)^5 \right]. \quad (1)$$

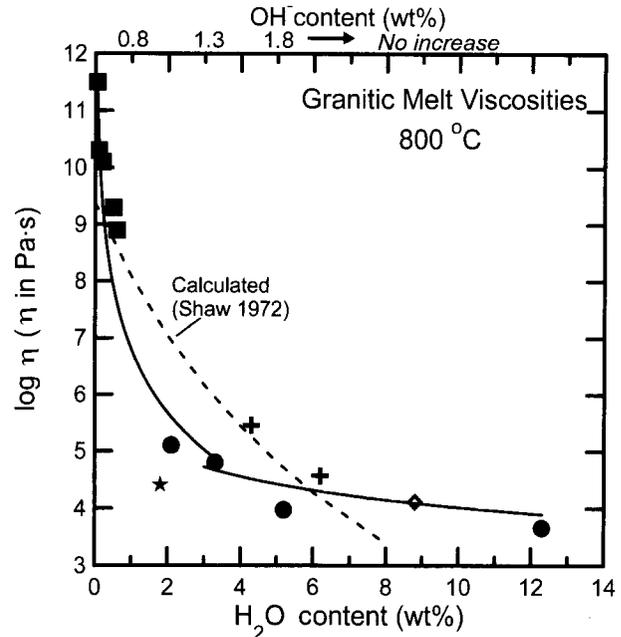


FIGURE 1. Viscosity of granitic melts vs. dissolved H₂O, in weight percent, at 800 °C. Plotted along the bottom axis is total H₂O content, and along the top axis is the estimated OH⁻ concentration based on infrared measurements of quenched, hydrous, granitic composition glasses by Silver et al. (1990). Measurements are as follows: squares, Friedman et al. (1963); circles, Persikov (1991); crosses, Shaw (1963); open diamond, Burnham (1964); and star, this study. Typical errors in viscosity measurements, 10–15%, are the same size or smaller than the symbols. The dashed line corresponds to viscosities calculated by the technique of Shaw (1972) for the composition studied by Persikov (1991). The solid lines represent two power-law fits to measured viscosities, one for melts with 0–3.3 wt% H₂O and one for melts with 3.3–12.3 wt% H₂O.

Propagation of experimental errors results in estimated uncertainties of ±15% (relative) for all viscosity measurements. Previous studies in this laboratory have demonstrated that our average reproducibility of hydrous melt viscosities measured with the same technique is within 13% (relative) (Baker and Vaillancourt 1995).

The viscosity of the anhydrous albitic melt at 1400 °C, 1.5 GPa, is 1060 Pa·s, which agrees within error with the albitic melt viscosity measured by Breatly and Montana (1989), 1088 Pa·s, but is significantly lower than Kushiro's (1978) measurements of 2600 Pa·s. Addition of 0.5 wt% H₂O lowers the viscosity of this melt by approximately an order of magnitude to 116 Pa·s.

The viscosity of the granitic melt with 1.8 wt% H₂O at 800 °C, 1.0 GPa, is 25748 Pa·s. This viscosity is lower by approximately a factor of five than the viscosity of a granitic melt with 2.1 wt% H₂O measured at 50 MPa by Persikov (1991) but is similar to the viscosities of granitic melts with 5–9 wt% H₂O measured by Persikov (1991), Shaw (1963), and Burnham (1964) (Table 2, Fig. 1). Viscosity determinations at lower H₂O contents were not

attempted because the estimated minimum time necessary (using the models described below) to make the measurement using the falling-sphere method for a granitic melt with 1 wt% H₂O at 800 °C is in excess of 2000 h.

THE EFFECT OF H₂O ON GRANITIC MELT VISCOSITIES

Viscosities measured in this study have been combined with measured viscosities of albite melt at 1.5 GPa and 1400 °C (Dingwell and Mysen 1985) and measured viscosities of granitic melts at 785–800 °C and pressures from 1 atm to 740 MPa (Tables 1 and 2). Plotting viscosity vs. the weight-percent H₂O dissolved in the melt demonstrates that addition of 2 wt% H₂O results in a six order-of-magnitude decrease in melt viscosity (Fig. 1). Additional dissolved H₂O, up to 12 wt%, results in an additional factor of 30 decrease in the viscosity (Fig. 1). The rapid decrease in viscosities has been attributed to the observation that at low total H₂O concentrations the predominant hydrous species in the melt is OH⁻ (Stolper 1982; Silver et al. 1990). The OH⁻ species interacts strongly with the silicate melt and either depolymerizes the melt through the breaking of Si-O-Si bonds (e.g., Sykes and Kubicki 1993) or simply weakens some Si-O-Si bonds without depolymerization (Kohn et al. 1989). Either mechanism significantly affects melt structure and results in the observed orders-of-magnitude decrease in viscosity when only a few weight-percent H₂O is added to the melt (Stolper 1982). At higher water concentrations the predominant hydrous species is molecular H₂O, which interacts weakly with Si-O-Si bonds and has little effect on melt viscosity (Stolper 1982). One anomalous viscosity measurement exists of a granitic melt with 4.3 wt% H₂O (Shaw 1963), which is higher than viscosities of melts of similar composition and with lower dissolved H₂O concentrations (Fig. 1). Because of this discrepancy it was decided not to use this datum in the viscosity models. Measured viscosities were fit with two power-law curves. One curve was fitted to melts with up to 3.3 wt% H₂O and the other to melts with greater than or equal to 3.3 wt% H₂O. These empirical fits to the data intersect at an H₂O concentration of near 3 wt%, where Silver et al. (1990) demonstrated that the concentration of OH⁻ species becomes saturated in granitic melts and does not increase (Fig. 1, top horizontal axis). Such an H₂O content is nearly equivalent to a mole fraction of total dissolved H₂O, $X_{\text{H}_2\text{O}}^{\text{tot}}$, in albite melt of 0.3, the concentration at which Sykes and Kubicki (1993) suggested that a change in the H₂O dissolution mechanism occurs. For comparison, viscosities of the granitic melt studied by Persikov (1991) have been calculated using the model of Shaw (1972) at various H₂O contents. The calculated viscosities are similar to measured viscosities at H₂O concentrations between 5 and 7 wt%, but the calculations overestimate viscosities by one to two orders of magnitude at lower H₂O contents and underestimate viscosities by similar values at higher H₂O contents (Fig. 1). Although the empirical power-law fits provide a superior means of predicting gran-

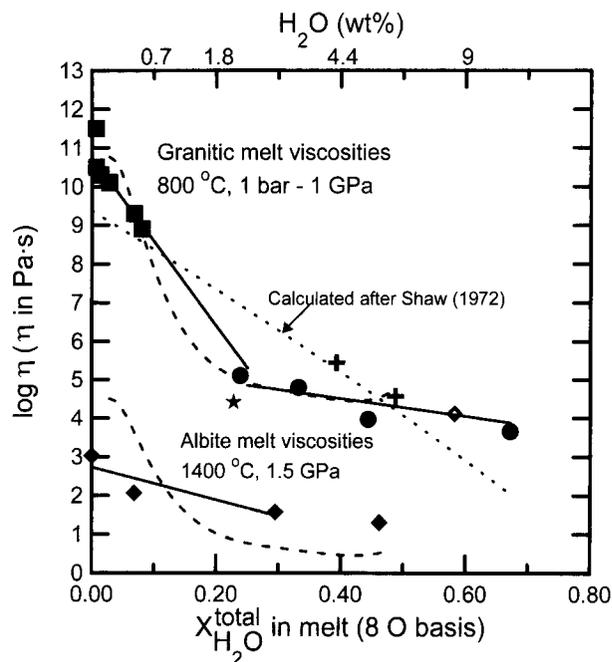


FIGURE 2. Viscosity of granitic and albite melts vs. mole fraction of total dissolved H₂O used to calibrate viscosity models. Molecular weight of anhydrous granitic melts was calculated on the basis of eight O atoms following Burnham (1979). Symbols are measured viscosities from the same sources as in Figure 1 with the exception of the solid diamonds, which are measured viscosities of albite melt (discussed in text). Solid lines are piecewise, log-linear fits to the data from the empirical model, which yield Equations 3 and 4 in the text. Dashed lines are the best fit of the configurational entropy model based on Equation 8 to viscosity data in this figure. The dotted line is the calculated viscosity of Persikov's granite (1991) following the method of Shaw (1972).

itic melt viscosities at 800 °C, they cannot be extrapolated to calculate melt viscosities at other temperatures.

CREATION AND CALIBRATION OF THE EMPIRICAL MODEL

The power-law fits (Fig. 1) intersect at the H₂O content at which Sykes and Kubicki (1993) proposed that a change in the H₂O solubility mechanism for albite melt occurs, indicating that consideration of H₂O solubility in granitic melts on a molar basis with albite-equivalent, eight O atoms would be informative. Molecular weights of the granitic melts were calculated on the basis of eight O atoms following Burnham (1979) and using a computer program written by D.H. Egger (1984 personal communication). When viscosities are plotted vs. the mole fraction of H₂O the data form two arrays, one for $X_{\text{H}_2\text{O}}^{\text{tot}} < 0.3$ and one for $X_{\text{H}_2\text{O}}^{\text{tot}} > 0.3$. Each array is easily fit to equations of the form (Fig. 2)

$$\log \eta = AX_{\text{H}_2\text{O}} + B \quad (2)$$

where A is the slope of the correlation line and B the intercept. One line is fit to the viscosities of melts with $X_{\text{H}_2\text{O}}^{\text{tot}}$ concentrations up to 0.332, and the other line is fit

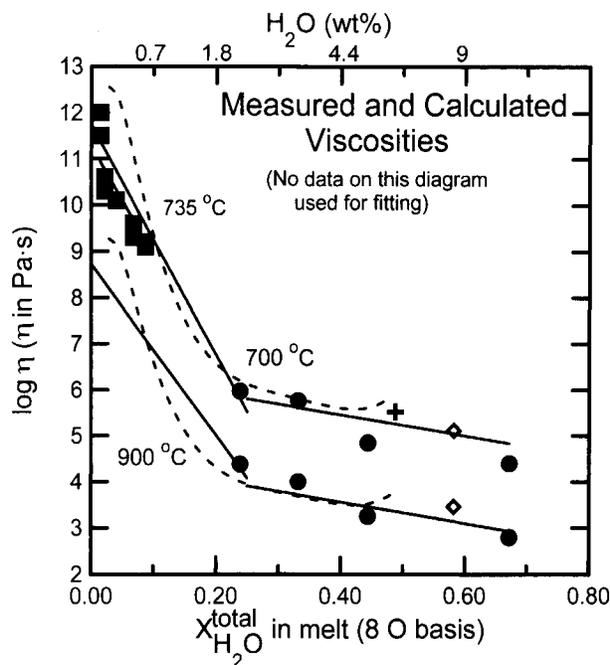


FIGURE 3. Calculated and measured viscosities of granitic melts at 700 and 900 °C. Symbols are measured viscosities from the same sources as in Figures 1 and 2 (see Fig. 1 and Table 2 for data sources). Solid lines are calculated viscosities using the empirical model (Eqs. 3 and 4), and dashed lines are calculated with the configurational entropy model (Eq. 8).

to melts with higher concentrations of dissolved H_2O (Fig. 2). This piecewise, log-linear fit to the viscosity data was chosen because it is the most simple function that empirically describes the data and can be easily extrapolated to calculate granitic melt viscosities at other temperatures. The piecewise fitting of the data is an oversimplification of the observed effect of H_2O on granitic melt viscosity (Figs. 1 and 2). The measured viscosities could be fit with a spline curve, however the nature of such a fitted curve makes it difficult, if not impossible, to extrapolate for calculation of viscosities at other conditions. Following the accepted assumption that albite provides an analog to granitic melts (e.g., Burnham 1979; Hochella and Brown 1984; Persikov 1991), the albite viscosities measured in this study at 1.5 GPa, 1400 °C, together with a viscosity determined by Dingwell and Mysen (1985) at the same conditions but with 2.79 wt% dissolved H_2O were plotted and fitted with Equation 2. As is evident in Figure 2, at low total H_2O concentrations the slope of the correlation line between viscosity and H_2O content is significantly different for the albite melt at 1.5 GPa, 1400 °C, and for the granitic melts at pressures between 1 atm and 1.0 GPa and temperatures between 785 and 800 °C. This difference indicates that addition of small, equivalent amounts of H_2O is more effective in reducing granitic melt viscosities at ~ 800 °C than albite melt viscosities at 1400 °C. Differences in these slopes are due to the different pressures, temperatures, and melt compositions. Pre-

vious viscosity studies indicated that pressure effects between 500 MPa and 1.5 GPa would be less than a factor of three (Kushiro 1978; Scarfe et al. 1987). Composition affects melt viscosities (cf. Shaw 1972), however viscosities of anhydrous albitic and granitic melts are similar to one another (Hochella and Brown 1984). Thus, it appears that the dominant effect responsible for the difference in slope between the correlation lines for viscosity and $X_{H_2O}^{tot}$ at low H_2O contents is temperature. To model the viscosities of low H_2O -content granitic melts, $X_{H_2O}^{tot} \leq 0.25$, the slopes of the log-linear correlation line between granitic melt viscosity and $X_{H_2O}^{tot}$ at 800 °C and the log-linear correlation line between albitic melt viscosity and $X_{H_2O}^{tot}$ at 1400 °C were fitted with a linear model. This model can be used to calculate the slope of the log-linear correlation line between granitic melt viscosities and $X_{H_2O}^{tot}$ for low H_2O -content melts at magmatic temperatures but requires anhydrous viscosities to constrain the intercepts of these correlation lines with the viscosity axis. Viscosities of the anhydrous granitic melt measured by Murase and McBirney (1973) at 700 and 900 °C were used as the intercepts of the correlation lines. This empirical fit allows calculation of the viscosities of granitic melts with low concentrations of H_2O , $X_{H_2O}^{tot} \leq 0.25$, at different temperatures (Fig. 3).

Comparison of the viscosities of H_2O -rich melts, $X_{H_2O}^{tot} > 0.25$, at 700 and 900 °C with those at 800 °C indicates little difference in the slopes of the log-linear correlations (Figs. 2 and 3). If the slope of the correlation between viscosity and $X_{H_2O}^{tot}$ at high H_2O concentrations is temperature independent between 900 and 700 °C, only the intercepts for the correlations at 900 and 700 °C need to be determined. These intercepts were determined by assuming that their change with temperature should be equivalent to the change in the anhydrous viscosities with temperature. Using the difference between the anhydrous granitic melt viscosities measured at 700 and 800 °C (Murase and McBirney 1973), $\Delta \log \eta = 2.19$, as a correction term to the intercept calculated from the experimental data at 800 °C results in the following equations for the calculation of granitic melt viscosities at temperatures between 700 and 900 °C (plotted in Fig. 3): For $X_{H_2O}^{tot} \leq 0.25$,

$$\log \eta = (0.0292649T - 53.198903)X_{H_2O}^{tot} - 0.0129207T + 24.2973 \quad (3)$$

and for $X_{H_2O}^{tot} > 0.25$,

$$\log \eta = -2.2977826X_{H_2O}^{tot} - 0.0095110T + 15.6293 \quad (4)$$

where viscosity is given in pascal-seconds, temperature, T , is in kelvins, and the mole fraction of H_2O is calculated on the basis of eight O atoms for the anhydrous melt composition. The number of digits in Equations 3 and 4 do not reflect precision but are retained to minimize rounding errors. For most granitic compositions a molecular weight of 260 g/mol can be used to determine the mole fraction of H_2O in the melt with no significant loss of accuracy in the calculated viscosity. The viscosities

calculated by this model reproduce the measured viscosities excellently (Figs. 2 and 3). The average difference between measured and calculated viscosities is -0.03 log units. This results in an average difference between measured and calculated viscosities of $<10\%$ or approximately the same as typical errors in the original viscosity measurements (Shaw 1963; Burnham 1964; Persikov 1991; this study).

A MODEL OF HYDROUS GRANITIC MELT VISCOSITIES BASED ON CONFIGURATIONAL ENTROPY THEORY

Many theoretical models exist to explain viscous transport in silicate melts (Bottinga et al. 1995). Perhaps the most successful of these is the configurational entropy theory that relates viscosity to the number of configurational states available to the liquid (Adam and Gibbs 1965; Richet 1984; Bottinga et al. 1995). This model has quantitatively explained viscosities of single-component silicate melts (e.g., diopside) and qualitatively explained viscosities of binary silicate melts (Richet 1984; Bottinga et al. 1995). These previous successes were the inspiration to fit the viscosity equations of configurational entropy theory to measured viscosities of granitic melts at 800°C and albite melt at 1400°C and then to test the fit by calculating viscosities of granitic melts at 900 and 700°C . Following configurational entropy theory the viscosity of a liquid is given by (Adam and Gibbs 1965; Richet 1984; Bottinga et al. 1995)

$$\eta = A_e \exp\left(\frac{B_e}{TS_{\text{conf}}}\right) \quad (5)$$

where A_e and B_e are constants derived from viscosity measurements, T is the temperature in kelvins, and S_{conf} is the configurational entropy of the melt. For some single-component compositions S_{conf} is calculated from calorimetric measurements (Richet 1984), and in other cases S_{conf} is calculated by fitting the above equation to viscosity data (Richet 1984; Bottinga et al. 1995). For mixtures composed of multiple components the configurational entropy of the mixture relative to the pure end-member components, $\Delta S_{\text{conf}}^{\text{mix}}$ can be calculated by (cf. Eq. 13, Richet 1984)

$$\Delta S_{\text{conf}}^{\text{mix}} = -R \sum X_i \ln X_i \quad (6)$$

where R is the gas constant and X_i is the mole fraction of the component in the mixture. Therefore, for a multicomponent system such as granitic melt + H_2O the viscosity at any temperature can be described by

$$\eta = A_e \exp\left[\frac{B_e}{T(\sum X_i S_{\text{conf},i} + \Delta S_{\text{conf}}^{\text{mix}})}\right] \quad (7)$$

where $S_{\text{conf},i}$ is the configurational entropy of each component in the mixture, and ΔS_{conf} is the configurational entropy due to mixing of the components as defined by Equation 6. Components can be defined as mineral compositions (e.g., albite and orthoclase) or by the structural

units present in the melt. Defining the components and their mole fractions in the mixture is, unfortunately, a difficult problem; this problem is especially acute in systems in which species undergo disproportionation reactions. Such reactions have been observed in silicate melts by nuclear magnetic resonance spectroscopy, where, for example, two SiO_4 tetrahedra with three bridging O atoms (Q^3) may react to form a tetrahedral unit with two bridging O atoms (Q^2) and another with four bridging O atoms (Q^4) (e.g., Stebbins 1988).

Equation 7 was to fit the viscosity measurements at 800 and 1400°C to calibrate the configurational entropy model. The least-squares fitting was performed using a quasi-Newton minimization method in the software package SYSTAT (Wilkinson 1989). An additional viscosity datum for albite melt with 5.58 wt% H_2O at 1.5 GPa, 1400°C , extrapolated from lower temperature measurements of Dingwell (1987), was needed to calibrate the configurational entropy model. Attempts to model the effects of H_2O on granitic melt viscosities by use of a binary $X_{\text{H}_2\text{O}}^{\text{gr}}-\text{silicate}$ melt mixture, as was used in the empirical model, were unsuccessful. The lack of success is attributed to the observation that hydrous silicate melts are, at the very least, a ternary mixture of molecular H_2O , OH^- , and silicate melt (cf. Stolper 1982). Additionally, disproportionation of silicate species discussed above can significantly increase the number of components in the melt. Because of the uncertainty of the nature of the silicate melt speciation, hydrous melts were modeled as a ternary mixture of H_2O , OH^- , and silicate melt. The mole fractions of H_2O and OH^- were estimated using the measured concentrations of OH^- and H_2O rhyolitic glasses hydrated with up to approximately 6 wt% total H_2O at 850°C (Silver et al. 1990) and fitted with polynomial expressions applicable to anhydrous melts with molecular weights of 260 g/mol: $X_{\text{H}_2\text{O}} = 4.073 \times 10^{-4} (\text{wt}\% \text{H}_2\text{O})^4 - 6.514 \times 10^{-3} (\text{wt}\% \text{H}_2\text{O})^3 + 3.226 \times 10^{-2} (\text{wt}\% \text{H}_2\text{O})^2 + 1.096 \times 10^{-2} (\text{wt}\% \text{H}_2\text{O}) - 3.680 \times 10^{-4}$, and $X_{\text{OH}^-} = -1.024 \times 10^{-3} (\text{wt}\% \text{H}_2\text{O})^4 + 1.696 \times 10^{-2} (\text{wt}\% \text{H}_2\text{O})^3 - 1.022 \times 10^{-1} (\text{wt}\% \text{H}_2\text{O})^2 + 2.67 \times 10^{-1} (\text{wt}\% \text{H}_2\text{O}) + 7.213 \times 10^{-4}$. The H_2O speciation estimations are only approximations because any effects of temperature and pressure are ignored, and the concentrations measured in the quenched glasses are assumed to be equivalent to those in the melts, even though this equivalence is not strictly correct (Silver et al. 1990; Y. Zhang 1993 personal communication). To fit an equation to the measured viscosities at 800 and 1400°C it was necessary to consider the configurational entropy term in Equation 7, $\sum X_i S_{\text{conf},i}$, as a single variable weighted by the mole fraction of the silicate melt and to multiply each $X_i \ln X_i$ term by a constant. The resulting equation is

$$\ln \eta = A_e + \frac{B_e}{T[S_{\text{conf}}(X_{\text{silicate melt}}) - R \sum C_i X_i \ln X_i]} \quad (8)$$

where T is in kelvins; R is the gas constant, 8.314 J/(mol·K) and parameters A_e , B_e , S_{conf} , $C_{\text{H}_2\text{O}}$, C_{OH^-} , and $C_{\text{silicate melt}}$ were determined by fitting this equation to measured vis-

cosities. The fitted parameters for the ternary mixing model are $A_e = -15.398$, $B_e = 181.622$, $S_{\text{conf}} = 4.567 \times 10^{-3}$, $C_{\text{H}_2\text{O}} = -1.899 \times 10^{-3}$, $C_{\text{OH}^-} = -1.531 \times 10^{-3}$, and $C_{\text{silicate melt}} = 4.913 \times 10^{-3}$.

The ability of this equation to reproduce the data to which it is fitted is displayed in Figure 2, and its predictive power for the estimation of viscosities at other temperatures is displayed in Figure 3, where calculated viscosities are plotted against $X_{\text{H}_2\text{O}}^{\text{qt}}$ (calculated without dissociation into OH^- for comparison with the empirical model above). The configurational entropy model accurately reproduces hydrous granitic melt viscosity data at 800 °C from 0.5 wt% total H_2O to its upper limit of applicability, approximately 6 wt% total H_2O . The average difference between measured and calculated viscosities is -0.2 log units. However, as is obvious from Figure 2, the fit to the hydrous albitic melt viscosities at 1400 °C is poor with some differences between measured and calculated viscosities exceeding an order of magnitude. Despite the poor fit to the high-temperature albite data, the configurational entropy model is successful at reproducing measured viscosities at 900 and 700 °C to almost within error of measurement, except for extremely low H_2O contents, less than 0.5 wt%, at 735 °C, where calculated viscosities can be an order of magnitude higher than measured viscosities. Inflections occur at each end of the calculated curve of viscosity vs. H_2O content and indicate the danger of extrapolating the equation outside the range of available viscosity and $X_{\text{H}_2\text{O}}-X_{\text{OH}^-}$ speciation data.

The values of the parameters in Equation 8 are derived from the fit to that equation to the data and have no physical significance. For example, directly determined configurational entropies in single-component silicate melts are orders of magnitude larger than those in Equation 8 (Richet 1984; Bottinga et al. 1995). This difference suggests that S_{conf} in Equation 8 should be considered as only a mathematical parameter that does not reflect the configurational entropy of the melts studied. Furthermore, the simplifying assumptions used to fit Equation 8 to the data, such as the ternary $\text{H}_2\text{O}-\text{OH}^-$ -silicate melt mixing model (which neglects possible disproportionation reactions in the silicate melt) or the assumption that the OH^- - H_2O speciation measured in glasses (as opposed to melts) at a single temperature is applicable for all conditions considered, limit the physical significance of the parameters to the extent that the assumptions used in constructing the model are correct. It is certain that application of another mixing model with additional species or different OH^- - H_2O speciation information would affect all fitted parameters in Equation 8.

Despite the above caveats, the success of Equation 8 in modeling hydrous granitic melt viscosities is very encouraging and provides support for the configurational entropy theory of viscous transport. This success buttresses previous research that applied configurational entropy theory successfully to anhydrous silicate melts of geological importance (Richet 1984; Bottinga et al. 1995).

However, rigorous application of configurational entropy theory to hydrous granitic melt viscosities will require an accurate understanding of the thermodynamics of such systems.

COMPARISON OF EMPIRICAL AND CONFIGURATIONAL ENTROPY MODELS FOR CALCULATION OF GRANITIC MELT VISCOSITY

Both models for the calculation of granitic melt viscosity presented in this work provide adequate estimates of melt viscosities for petrological calculations. Both models produce similar estimated viscosities at H_2O contents between ~ 2 and 6 wt% (Figs. 2 and 3). Between 0 and ~ 0.5 wt% H_2O the configurational entropy model yields viscosities up to an order of magnitude above the empirical model and measured melt viscosities. Between ~ 1 and ~ 2 wt% H_2O the configurational entropy model calculates viscosities up to an order of magnitude below the empirical model, but no experimental data exist in this region for comparison. The configurational entropy model is based on a generally accepted theory that has repeatedly demonstrated its success in modeling the viscosities of anhydrous melts (Richet 1984; Bottinga et al. 1995). However, this model suffers from our lack of knowledge of silicate melt speciation and accurate molecular H_2O and OH^- concentrations in silicate melts. Although configurational entropy theory promises a better understanding of hydrous silicate melt dynamics and chemistry, our current knowledge of silicate melt structure only allows us to demonstrate that viscosity measurements of hydrous granitic melts are consistent with theory. Although the empirical model has no theoretical justification, it exhibits a smaller difference between measured and calculated viscosities, -0.03 log units, compared to the configurational model, -0.2 log units, which demonstrates the superior accuracy of the empirical model.

EFFECT OF PRESSURE ON VISCOSITIES OF HYDROUS GRANITIC MELTS

The hydrous granitic melt viscosities shown in Figure 2 were measured at pressures between 0.1 MPa (1 atm) and 1.5 GPa. Although this pressure range spans four orders of magnitude, the effect of pressure on viscosity is minor. At high H_2O contents, 8.8 wt% H_2O , Burnham (1964) found no effect of pressure on the viscosities of the melt he investigated. Although Persikov's (1991) experiments at various pressures were not at constant H_2O concentration but varied from 3.3 wt% H_2O (at 100 MPa) to 12.3 wt% H_2O (at 700 MPa), he demonstrated that viscosities of granitic melts diminished by only 30% between 100 and 700 MPa (Table 2). This decrease in viscosity is attributed entirely to the addition of H_2O , but if the effects of H_2O are neglected then these data indicate that an increase in pressure from 100 to 700 MPa could decrease granitic melt viscosities by only 30%.

At low H_2O contents pressure may have a greater effect on melt viscosities than at high H_2O contents. Comparison of the granitic melt viscosity measured in this study

at 1.0 GPa, 800 °C, and that measured by Persikov (1991) at 50 MPa, 800 °C (Figs. 1 and 2; Table 2), suggests that viscosities of granitic melts with near 2 wt% H₂O could decrease by a factor of five over this pressure range. An argument against such a large pressure effect is the observation that the viscosity of albite melt with 1.9 wt% H₂O is 2884 Pa·s at 50 MPa, 1250 °C, and 2239 Pa·s at 400 MPa, 1200 °C (Persikov 1991). Although the measurements are not isothermal, the small difference in the viscosities, ~22%, indicates that the effects of crustal pressures on the viscosity of hydrous melts is minor. Nevertheless, application of this viscosity model to low H₂O-content granitic melts at pressures of 1.0 GPa and higher requires caution but should yield calculated viscosities that are within a factor of five of the real viscosities

EFFECT OF COMPOSITION ON GRANITIC MELT VISCOSITIES

Compositions of the melts used for this study are peraluminous and metaluminous granites (rhyolites) and albite ranging from 69 (albite) to 76 wt% SiO₂ (Table 1). The excellent fit of the models to the data discussed previously indicates that the proposed models for calculation of melt viscosities should be applicable to most per- and metaluminous granites. Application of either of the proposed models yields viscosities for the anhydrous rhyolitic melt, 72 wt% SiO₂, studied by Hochella and Brown (1984) within 0.3 log units of the measured value at 1200 °C, the lowest temperature they investigated. Estimated viscosities of the anhydrous dacitic melt, 67 wt% SiO₂, studied by Stein and Spera (1993) at 1000–1050 °C are typically 1.4 log units too high using the empirical model and 0.6 log units too high using the configurational entropy model. Thus, these models are probably applicable to granitic magmas with silica contents as low as 70 wt% and can provide reasonable estimates, within approximately an order of magnitude, of the maximum possible viscosity for hydrous per- and metaluminous rhyodacitic and dacitic melts. However, these models should not be used for the calculation of peralkaline melt viscosities because Baker and Vaillancourt (1995) demonstrated that with the same total concentration of volatiles, H₂O + F, viscosities of peralkaline granitic melts are only one-fifth the viscosities of compositionally similar per- and metaluminous granitic melts.

IMPLICATIONS FOR THE PETROGENESIS OF GRANITIC MAGMAS

The viscosities of low H₂O-content granitic melts calculated by these models are one to two orders of magnitude below those calculated by Shaw's (1972) model. The lower viscosities result in substantially more rapid transport properties of low H₂O-content granitic melts than previously thought possible. Because most transport properties of silicate melts are inversely dependent upon viscosity, a decrease in viscosity by one order of magnitude results in an increase in the transport rate by an order of magnitude. One example of a viscosity-depen-

dent property is the settling velocities of crystals, v , as calculated by Stokes's law (Eq. 1, but without the Faxen correction):

$$v = \frac{1}{\eta} \frac{2g\Delta\rho r^2}{9}. \quad (9)$$

The new, low viscosities of granitic melts with only small amounts of H₂O calculated by the proposed models result in more rapid, and therefore efficient, crystallization fractionation of granitic magmas than previously considered possible. Another viscosity-dependent transport process is the separation of melt from residual crystals through gravitational compaction as modeled by McKenzie (1985). This separation velocity, w_0 , is given by McKenzie's (1985) Equation 2:

$$w_0 = \frac{1}{\eta} \frac{k_\phi(1-\phi)(\rho_s - \rho_l)g}{\phi} \quad (10)$$

where k_ϕ is the permeability, ϕ is the porosity or fraction of partial melt, ρ_s is the density of the crystalline solid, ρ_l is the density of the melt, g is Earth's gravity, and η is the melt viscosity. For a fixed permeability and melt fraction this equation demonstrates an order-of-magnitude increase in separation velocity for each order-of-magnitude decrease in melt viscosity. Although gravitational compaction is probably not the only mechanism responsible for separation of granitic melts from their crustal source regions (Sawyer 1991), the velocities of melt separation remain inversely proportional to melt viscosity. Calculated fluxes of segregated melt batches through dikes are also strongly affected by melt viscosity. Although our knowledge of transport rates in dikes is limited, a simplistic model for calculating the mass flux, G , of melts through volcanic conduits of circular cross section displays a similar dependency on melt viscosity (Jaupart and Tait 1990):

$$G = \frac{1}{\eta} \frac{\rho_l \pi R^4}{8H} [\Delta P + (\rho_s - \rho_l)gH] \quad (11)$$

where R is the radius of the conduit, H is the height of the conduit, and ΔP is the pressure difference between the bottom and the top of the conduit. The rates of separation and ascent through dikes of low-H₂O granitic melts are much more rapid than previously thought possible because of the lower viscosities calculated by the proposed models. Ascent of granitic diapirs through the crust depends upon the rheology of the deforming region of country rock immediately surrounding the ascending diapir (Mahon et al. 1988). The calculations of Mahon et al. (1988) for the rheology of the deformation region used Shaw's (1972) method for calculating granitic melt viscosities. Although diapir ascent viscosities were not calculated in this study, substitution into the Mahon et al. (1988) calculations of partially molten country rock viscosities estimated by the methods proposed in this work would increase diapiric ascent rates and decrease the depth of final diapir emplacement (cf. Mahon et al. 1988).

The empirical and configurational entropy models presented in this work are significant improvements over previous models for the prediction of the viscosities of granitic melts containing small amounts of H₂O (<4 wt%). Viscosities of low H₂O-content melts calculated by either of the two new models are orders of magnitude less than previously calculated (e.g., Shaw 1972) and are in agreement with measured viscosities at low H₂O contents. These lower viscosities result in orders-of-magnitude increases in virtually all melt-transport processes occurring in granitic magmas.

ACKNOWLEDGMENTS

J. Vaillancourt is thanked for the measurements of the albitic and granitic melt viscosities. Thorough and helpful reviews by Frank Spera and Michael Ryan resulted in an improved paper. This research was supported by the Natural Sciences and Engineering Research Council of Canada (OGP0089622) and by Employment Canada.

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