The viscosity of planetary tholeiitic melts: A configurational entropy model

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Abstract

The viscosity (η) of silicate melts is a fundamental physical property controlling mass transfer in magmatic systems. Viscosity can span many orders of magnitude, strongly depending on temperature and composition. Several models are available that describe this dependency for terrestrial melts quite well. Planetary basaltic lavas however are distinctly different in composition, being dominantly alkali-poor, iron-rich and/or highly magnesian. We measured the viscosity of 20 anhydrous tholeiitic melts, of which 15 represent known or estimated surface compositions of Mars, Mercury, the Moon, Io and Vesta, by concentric cylinder and parallel plate viscometry. The planetary basalts span a viscosity range of 2 orders of magnitude at liquidus temperatures and 4 orders of magnitude near the glass transition, and can be more or less viscous than terrestrial lavas. We find that current models under- and overestimate superliquidus viscosities by up to 2 orders of magnitude for these compositions, and deviate even more strongly from measured viscosities toward the glass transition.

We used the Adam–Gibbs theory (A–G) to relate viscosity (η) to absolute temperature (T) and the configurational entropy of the system at that temperature (S^{conf}), which is in the form of $\log\eta = A_e + B_e/TS^{\mathrm{conf}}$. Heat capacities ($C_P$) for glasses and liquids of our investigated compositions were calculated via available literature models. We show that the A–G theory is applicable to model the viscosity of individual complex tholeiitic melts containing 10 or more major oxides as well or better than the commonly used empirical equations. We successfully modeled the global viscosity data set using a constant A_e of -3.34 ± 0.22 log units and 12 adjustable sub-parameters, which capture the compositional and temperature dependence on melt viscosity. Seven sub-parameters account for the compositional dependence of B_e and 5 for S^{conf}. Our model reproduces the 496 measured viscosity data points with a 1σ root-mean-square deviation (rmsd) of 0.12 log units across 13 orders of measured melt viscosity. The model performed well in predicting the viscosity of lunar and martian melts not used in calibration, and should be used to calculate lava flow velocities and fluxes for anhydrous basaltic volcanism on other moons and planets.
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1. INTRODUCTION

The viscosity of silicate melts influences many processes in igneous petrology, including the rate of crystal growth, the rates of rise and settling of bubbles and crystals in magma, convection and mass transfers in magma chambers and volcanic plumbing systems, the eruption style of volcanoes, and the mode of lava emplacement. Lava viscosity must be known for various compositions at a range of temperatures, in order to model many processes in planetary sciences, such as velocity and flux during lava flow emplacement, embayment of ancient craters, or rille formation

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through thermal and mechanical erosion (Williams et al., 2001; Hurwitz et al., 2012; Byrne et al., 2013; Dundas and Keszthelyi, 2014). Viscosity can vary over many orders of magnitude during these geological processes, strongly depending on temperature and composition. The earliest efforts to predict the viscosity of multi-component silicate liquids as a function of composition and temperature assumed Arrhenian behavior at superliquidus conditions (Bottinga and Weill, 1972; Shaw, 1972). Viscosity data measured at subliquidus temperatures, near the glass transition, allowed the construction of empirical models considering non-Arrhenian behavior of silicate melts, parameterized by the Vogel-Fulcher-Tammann equation (Vogel, 1921). This VFT-equation has the form

$$\log \eta = A + B/(T - T_0) \tag{1}$$

where A, B and T_0 are adjustable parameters. Parameter A represents the limit of $\log \eta$ (Pa·s) extrapolated to infinite temperature, and T_0 is the temperature (K) at which viscosity becomes infinite. Parameter B represents the pseudo-activation energy associated with viscous flow, and is thought to represent a potential energy barrier obstructing the structural rearrangement of the melt (e.g. Russell et al., 2003). Several recent models are based upon this approach (Giordano and Dingwell, 2003; Giordano et al., 2006, 2008), or utilize more complex empirical formulations (Hui and Zhang, 2007).

Adam and Gibbs (1965) proposed that relaxation in glass-forming liquids takes place through configurational changes in a liquid. Higher temperatures result in greater configurational entropies (S^{conf}), as cooperative rearrangements of the structure can take place independently in smaller and smaller regions of the liquid. As a result, relaxation times of liquids thus decrease. Richet (1984) combined the Adam and Gibbs (1965) theory of relaxation with the Maxwell relation between relaxation and viscosity ($\tau_s = \eta_s/G_\infty$; Dingwell and Webb, 1989), to derive the equation

$$\log \eta = A_e + B_e/TS^{conf}, \tag{2}$$

where T is the temperature in Kelvin, with parameters A_e and B_e. Parameter A_e is analogous to the VFT equation (Eq. (1)). Toplis (1998) found that A_e was in the range -2.6 ± 1 log Pa s for silicate melts, varying as a linear function of B_e per tetrahedron. Russell et al. (2003) postulated that the high-T viscosities of silicate melts converge to a common value. They solved for optimal values of A_e, by fitting experimental data, and obtained values of $10^{-4.3}$ $^{\pm 0.74}$ Pa s for the VFT (Eq. (1)), and $10^{-32 \pm 0.66}$ Pa s, when using configurational entropy theory (Eq. (2)).

According to Eq. (2), the effective activation energy $B_e/S^{conf}(T)$ depends on the Gibbs free energy barriers that hinder cooperative rearrangements in the liquid to initiate viscous flow (Richet, 1984), and the variation in temperature of the configurational entropy. The latter controls the magnitude of non-Arrhenian behavior, and can be found at any temperature with reference to the calorimetric glass transition temperature (T_g)

$$S^{conf}(T) = S^{conf}(T_g) + \int_{T_g}^{T} C_P^{conf}/TdT \tag{3}$$

where C_P^{conf} is the configurational heat capacity, defined as:

$$C_P^{conf}(T) = C_{P,l}(T) - C_{P,g}(T_g), \tag{4}$$

where $C_{P,l}(T_g)$ is the isobaric heat capacity of the liquid at temperature T, and $C_{P,g}(T_g)$ the isobaric heat capacity of the glass at T_g. The glass transition temperature of silicate glasses normally takes place when the heat capacity of the glass reaches the Dulong-Petit harmonic limit of $3R$ J mol^{-1} K^{-1}, where R is the universal gas constant (Richet, 1984; Neuville and Richet, 1991). However, this harmonic limit can be reached at values below $3R$, as it is observed for hydrous melts (Bouhifd et al., 2006, 2013), haplogranitic melts rich in Li$_2$O, K$_2$O, or Rb$_2$O, (Toplis et al., 2001), and vitreous B$_2$O$_3$ (Haggerty et al., 1968).

Russell et al. (2003) applied the Adam and Gibbs (1965) theory to several natural basaltic compositions, Giordano and Russell (2007) to glass-forming liquids in the CAS, MAS, MCAS system. Both studies demonstrated that the Adam and Gibbs (1965) theory can fit viscosity data with a similar quality to fits using the empirical VFT equation. More recently, Mauro et al. (2009) further developed the Adam–Gibbs theory to derive a more general equation for melt viscosity, and demonstrated its superiority over both the VFT equation and other formalisms, such as the Avramov–Milchev equation (Avramov and Milchev, 1988):

$$\log \eta = A + \left(\frac{\tau}{T}\right)^{\alpha} \tag{5}$$

where A, τ, and α are fitting parameters.

In the geological sciences, viscosity values are commonly extracted from the MELTS algorithm (Ghiorso and Sack, 1995), which uses the viscosity model of Shaw (1972). But this model does not account for the non-Arrhenian behavior of fragile (non-Arrhenian) liquids, such as basalts. Sometimes lava viscosities are calculated using the model of Giordano et al. (2008), for which the calibration dataset included very few compositions relevant to magmatism on other terrestrial bodies.

The objectives for this study were (i) to measure the viscosity of several planetary lava compositions, (ii) to compare the experimental data to the predictions of existing models, and (iii) to derive a better model for tholeiitic melt viscosity as a function of composition and temperature, based on the Adam–Gibbs thermodynamic theory of relaxation.

2. METHODS

2.1. Sample synthesis and characterization

The anhydrous glasses listed in Table 1 were obtained via two methods. Three crystal-bearing lavas, a midcontinent flood basalt from the Chengwatana volcanics (Lev et al., 2012), an ocean island basalt erupted at Mauna Ulu, Kilauea volcano Hawaii (Robert et al., 2014), and Mt. Nyiragongo (DR of Congo) were collected, crushed and melted at 1600 °C for two hours in air, quenched to a glass, then crushed and remelted again to ensure complete chemical homogenization. In addition, two lavas were synthesized (see method for planetary analog materials below).