Earth and Planetary Science Letters 501 (2018) 202–212

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Towards a structural model for the viscosity of geological melts

D. Giordano [a,*], J.K. Russell [b]

[a] Earth Sciences Department, University of Turin, Via Valperga Caluso, 35, 10125 Turin, Italy
[b] Earth, Ocean & Atmospheric Sciences, The University of British Columbia, Vancouver, British Columbia, V6T 1Z4, Canada

ARTICLE INFO

Article history:
Received 9 February 2018
Received in revised form 7 August 2018
Accepted 17 August 2018
Available online xxxx
Editor: T.A. Mather

Keywords:
viscosity
silicate-melt
structure
Raman
model
volcanology

ABSTRACT

The viscosity of silicate melts is the most important physical property governing magma transport and eruption dynamics. This macroscopic property is controlled by composition and temperature but ultimately reflects the structural organization of the melt operating at the microscale. At present, there is no explicit relationship connecting viscosity to silicate melt structure and vice versa. Here, we use a single Raman spectroscopic parameter, indicative of melt structure, to accurately forecast the viscosity of natural, multicomponent silicate melts from spectroscopic measurements on glasses preserved on Earth and other planets. The Raman parameter is taken as the ratio of low and high frequency vibrational bands from the silicate glass by employing a green source laser wavelength of 514.5 nm ($R_{514.5}$). Our model is based on an empirical linkage between $R_{514.5}$ and coefficients in the Vogel–Fulcher–Tammann function for the temperature dependence of melt viscosity. The calibration of the Raman-based model for melt viscosity is based on 413 high-temperature measurements of viscosity on 23 melt compositions for which published Raman spectra are available. The empirical model obviates the need for chemical measurement of glass compositions, thereby, providing new opportunities for tracking physical and thermochemical properties of melts during igneous processes (e.g., differentiation, mixing, assimilation). Furthermore, our model serves as a milepost for the future use of Raman spectral data for predicting transport (and calorimetric) properties of natural melts at geological conditions (e.g., volatiles and pressure) and production.

1. Introduction

The viscosity of silicate melts is one of the most important physical properties governing magma transport and eruption dynamics. The viscosity (η) of natural silicate melts spans at least 16 orders of magnitude (10^{-2} to 10^{14} Pa s) reflecting the pronounced effects of temperature (T) and chemical composition (X). The effect of temperature is, itself, dependent on melt composition, and silicate melts can show nearly Arrhenian (strong melts) or strongly non-Arrhenian (fragile) behaviour (Toplis, 1998; Toplis et al., 1997; Russell et al., 2003). The accurate prediction of silicate melt viscosity as a function of geological conditions (T and X) is of paramount importance for modelling and understanding magmatic and volcanic processes.

Laboratory measurements have explored and elucidated the viscosity of silicate melts over virtually the full range of compositions and temperatures found on Earth (Giordano et al., 2008). The data have supported development of new models of melt viscosity (Table 1) that have different capacities for extrapolation and for prediction of other transport properties (e.g., Shaw, 1972; Bottinga and Weil, 1972; Russell and Giordano, 2005; Giordano and Russell, 2007; Hui and Zhang, 2007; Giordano et al., 2008; Whittington et al., 2009; Sehlke and Whittington, 2016). The majority of these models are purely empirical calibrations of viscosity measurements against the chemical composition of the melt and have no direct connection to melt structure.

Ultimately, viscosity is a macroscopic manifestation of the molecular structure and organization of the melt and is controlled by the degree and nature of polymerization (Bockris and Lowe, 1954; Lacy, 1965; Mysen et al., 1982). Providing a structural basis for predicting melt viscosity remains a seminal challenge in Earth Sciences (Richet and Bottinga, 1986, 1995; Richet and Neuville, 1992; Giordano et al., 2008). In simple chemical systems, the physical–chemical and transport properties are shown to be tied directly to melt structural properties (Bockris and Lowe, 1954; Lacy, 1965; Mysen et al., 1982; McMillan and Wolf, 1984; Bykov et al., 2009). Recently for example, Le Losq and Neuville (2017) following the work of others (Mysen, 1995) developed a model for melt viscosity in the simple system SiO_2–Na_2O–K_2O. Their 13-parameters model connects the transport and thermodynamic

* Corresponding author.
E-mail address: daniele.giordano@unito.it (D. Giordano).

https://doi.org/10.1016/j.epsl.2018.08.031
0012-821X/

Table 1
Summary of chemical models for geological melts.

Model source	Description	Model[a]	Melts (N)	Data (N)	Parameters
Shaw (1972)	Multicomponent, hydrous	A	–	120	25
Bottinga and Weill (1972)	Multicomponent	A	–	2440	∼34
Persikov (1991)	Multicomponent, hydrous	A (+P)	–	–	–
Baker (1996)	Granite melt, hydrous	NA, AG	1 (+H_2O)	34	6
Hess and Dingwell (1996)	Rhyolites, hydrous	NA	1 (+H_2O)	111	6
Giordano and Dingwell (2003)	Multicomponent anhydrous	NA, VFT	19	350	10
Russell and Giordano (2005)	An–Di–Ab system, anhydrous	NA, VFT	40	585	13
Giordano and Russell (2007)	CMAS system, anhydrous	NA, VFT	105	968	11
Hui and Zhang (2007)	Multicomponent, hydrous	NA	99	1451	37
Giordano et al. (2008)	Multicomponent, hydrous	NA, VFT	178	1770	17
Ardia et al. (2008)	Rhyolite, hydrous	NA, VFT (+P)	1 (+H_2O)	374	6
Whittington et al. (2009)	Dacite, hydrous	NA, VFT	1 (+H_2O)	76	6
Sehlke and Whittington (2016)	Planetary tholeiite basalt	NA, AG	20	496	13

[a] Abbreviations include: Arrhenian (A), Non-Arrhenian (NA), Pressure (P), Adam–Gibbs (AG), Vogel–Fulcher–Tammann (VFT).

properties of these simple melts explicitly to the structural state of the melt expressed via the abundances of Q^n-species recovered from Raman spectral analysis of the glasses.

Future progress in modelling the viscosity of multicomponent melts depends on our capacity to integrate the structural properties of melts into predictive models. Here, we present a first-order predictive model for melt viscosity based on a single parameter calculated from Raman spectra measured on the corresponding glasses. The intensity of different Raman lines relates to the identity and abundance of structural species in the glasses and, thus, informs on melt structural properties. On this basis, our empirical model explicitly links the structural properties of the multicomponent glasses to the viscosity of their corresponding melts.

Furthermore, this preliminary model suggests an alternative means of predicting or calculating melt viscosity that does not require chemical analysis of the melt's composition. The ability to estimate melt viscosity from a single Raman spectroscopic measurement of quenched glasses provides new opportunities to track the physical properties of melts (e.g. viscosity) throughout volcanological and petrological processes. For example, the proposed Raman-based viscosity model is ideal for situations where chemical measurements of quenched glasses are not feasible nor possible, or where the research questions require very large numbers of measurements or a continuous record of melt/glass compositions.

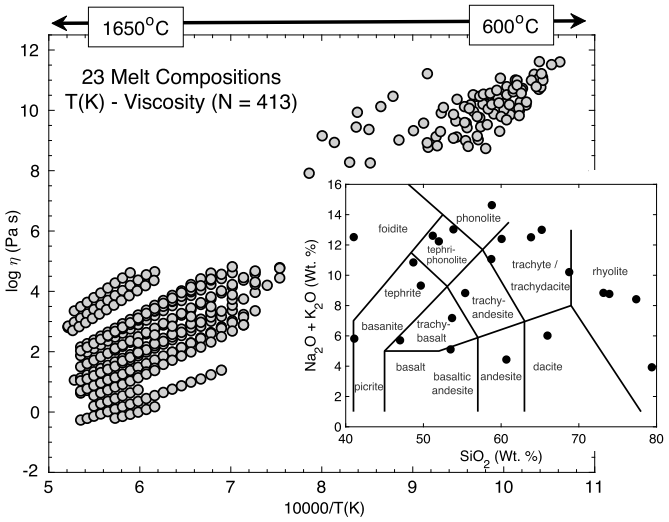

Fig. 1. Summary of data used in predictive model for melt viscosity based on Raman spectroscopic data. The suite of 413 measured values of melt viscosity for 23 multicomponent melts plotted against a reciprocal temperature T(K) spanning super-liquidus to near glass transition temperatures. The data illustrate the extreme range in melt viscosity arising from variations in T and composition. Inset is alkalies vs. SiO_2 diagram showing compositional range of the 23 melts.

2. Experimental database

We have compiled data on anhydrous silicate melts for which: i) compositions are known, ii) multiple viscosity–T(K) pairs are measured, and for which iii) published Raman spectral ratios are available (Table A1, Supplementary material). The data include 413 viscosity measurements on 23 melt compositions spanning most of the compositional range of natural terrestrial melts including: subalkaline, calc-alkaline, alkaline, and peralkaline melts (Fig. 1; Inset). The measured viscosities range from $\sim 10^{-0.2}$ to 10^{12} Pa s over a temperature interval of ∼600 to 1650 °C (Fig. 1). We have also compiled published ratios of the intensities of Raman spectra collected for glasses (Mercier et al., 2009, 2010) produced by quenching of the same 23 melts (Supplementary Table A1). Combined, this is the widest compositional range of melts for which the temperature dependence of viscosity is measured and the Raman spectra for the corresponding glass are measured. The database derives from >10 published papers (see Supplementary Table A1) and provides a basis for exploring the correlations between melt structures and physical properties.

3. Raman spectral analysis of glasses

Raman spectroscopy is a versatile non-destructive technique for probing the short-range structure of glasses and melts. Raman spectroscopy has a high-spatial resolution of 1–2 μm^2 but can also analyze large km-size targets (cf. Angel et al., 2012). Comprehensive reviews of the use of Raman spectroscopy in the earth and planetary sciences are provided by Simon et al. (2003), Tarcea et al. (2008), Rossano and Mysen (2012), and Angel et al. (2012). These reviews illustrate the broad range of applications of Raman spectroscopy for studying any optically accessible sample. Raman spectroscopy is also being used for in-situ measurements of glasses at high temperature and pressure and has the potential for remote use on planetary surfaces (e.g., Simon et al., 2003; Sharma et al., 2010; Klein et al., 2004; Malfait, 2018).

Raman analysis involves relatively straightforward sample preparation and portable, miniaturized Raman spectrometers are now becoming available (e.g. Popp et al., 2002). Raman is highly suitable for studying natural glassy products (e.g., volcanic ash, pumice, scoria or obsidian) and has been used to estimate volatile contents and extents of iron oxidation in volcanic glasses (e.g., Mercier et al., 2009, 2010), and to estimate the composition of multicomponent silicate glasses (e.g. Di Genova et al., 2016). Although, it has not yet been used on molten lava, Sharma et al.'s (2010) work on minerals at high temperature (∼1003 K) and at target distances of ∼9 m, supports that potential. Raman has similar applications in industrial processes involving glassy or molten materials (e.g. Richet et al., 1993; Koroleva, 2017).