ARTICLE IN PRESS

Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Effect of oxygen fugacity on the glass transition, viscosity and structure of silica- and iron-rich magmatic melts

Danilo Di Genova[a,b,*], Jérémie Vasseur[b], Kai-Uwe Hess[b], Daniel R. Neuville[c], Donald B. Dingwell[b]

[a] School of Earth Sciences, University of Bristol, Wills Memorial Building, Queens Road, Bristol BS8 1RJ, UK
[b] Department of Earth and Environmental Sciences, Ludwig-Maximilians-Universität München, Theresienstrasse 41/III, 80333 München, Germany
[c] Géomatériaux, CNRS-IPGP UMR 7154, Paris Sorbonne Cité, 1 rue Jussieu, 75005 Paris, France

ARTICLE INFO

Keywords:
Iron-bearing glasses
Glass transition
Viscosity
Structure
Raman spectroscopy

ABSTRACT

Iron oxidation state affects the physical properties and structure of natural melts and, ultimately, magmatic and volcanic processes such as magma transport and eruptive style. Here, we study the glass transition temperature and melt viscosity of an iron-rich peralkaline rhyolite as a function of the iron oxidation state. Glass transition temperature is determined using a differential scanning calorimetry up to 680 °C. High-temperature viscosity is measured at 1385 °C using the concentric cylinder technique. Both the glass transition temperature and viscosity increase with oxygen fugacity conditions. Although significant changes in structure with temperature are expected, we observe a direct relationship between the effect of oxygen fugacity on bulk properties at high and low temperature and polymerization of glass structure as inferred by Raman spectroscopy. Our results show that viscosity models should consider the effect of oxygen fugacity on the melt viscosity at eruptive temperature together with the effect of water and crystal content.

1. Introduction

The structure of a naturally-occurring silicate melt governs its viscosity, which, in turn, influences magma ascent, degassing rate and, ultimately, eruption style of volcanoes [1,2]. Iron is a major component of natural melts coexisting in both reduced (Fe_2O) and oxidized (Fe_2O_3) states with coordination environments ranging from 4-fold, through 5-fold to 6-fold depending on the melt composition, temperature and oxygen fugacity [3–8]. Because of its unique and complex role in the melt structure, iron plays a crucial role and affects the transport of silicate melts [9–15].

While the structural role (i.e. network former vs network modifier) of iron is still highly debated [e.g., 6,8,16,17], it is generally accepted that increasing Fe_2O_3 content leads to an increase in viscosity of geologically relevant melts [14,15,18]. In this respect, Kremers et al. [19] have recently inferred that change in the iron oxidation state of basaltic-andesitic products influences melt viscosity, glass transition temperature (T_g), and ultimately eruptive dynamic of Mt. Yasur volcano (Vanuatu). However, so far, systematic studies of the effect of iron oxidation state on viscosity at high temperature, glass transition temperature (T_g) and melt structure were performed on simplified and/or silica-poor systems not at eruptive temperatures.

In this study, we present viscosity and glass transition measurements of an iron- alkali-rich rhyolite (pantellerite) under different redox conditions. The combination of these data allows us to explore the effect of iron oxidation state on melt viscosity at eruptive temperature. The wide range of eruptive styles [20] and the extremely high iron content (~9 wt%) make pantelleritic melt the most suitable candidate to study the effect of the iron oxidation state on bulk properties. Further, we correlate the glass structure as inferred by Raman spectra (from Di Genova et al. [21]) with the high temperature viscosity and glass transition temperature. To our knowledge, this is the first study presenting such a set of data for natural silicate melts and glasses. Finally, comparison of bulk properties and structure of quench products will lead to a better understanding of the temperature dependence of iron oxidation state during cooling.

2. Methodology

2.1. Starting material and viscosity measurements

The starting material consists of a homogenous and anhydrous pantellerite previously synthetized by Di Genova et al. [21]. In that study, the effect of iron oxidation state on the Raman spectra was studied and an empirical model for the estimation of $Fe^{3+}/Fe_{tot.}$ ratio in glasses was provided. In this study, we performed deconvolution of

---

[*] Corresponding author at: School of Earth Sciences, University of Bristol, Wills Memorial Building, Queens Road, Bristol BS8 1RJ, UK.
E-mail address: danilo.digenova@bristol.ac.uk (D. Di Genova).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.05.013
Received 18 February 2017; Received in revised form 19 April 2017; Accepted 10 May 2017

Please cite this article as: Di Genova, D., Journal of Non-Crystalline Solids (2017), http://dx.doi.org/10.1016/j.jnoncrysol.2017.05.013

Raman spectra previously published [21]. Therefore, Raman methodology is not reported.

High-temperature viscosity measurements were performed using a Brookfield DV-III+ viscometer head equipped with a concentric cylinder geometry. The viscometer was calibrated against a soda-lime-silica standard glass (DGG-1) following the method described by Dingwell [22]. The viscosity measurements were performed at 1385 °C and 1 atm under different oxygen fugacity conditions, using a gas-mixing furnace equipped with a gas-tight alumina muffle tube and CO-CO_2 gas mixing line (see Ref. [10] for details).

The oxygen fugacity $f(O_2)$ was controlled by CO-CO_2 gas mixtures and monitored by an yttrium-stabilized, zirconia-based oxygen electrode calibrated against air and pure CO_2. For each sample, a minimum of a day was required to permit melt equilibration with the experimental conditions (i.e. no viscosity change with time). The viscosity was measured initially in air and, afterwards, at more reduced conditions until $\log (fO_2) \approx -13$ (measured around the melt). The viscosity was recorded during the entire duration of the experiment at constant $f(O_2)$. The value was taken after 1 h of equilibrium conditions. During the measurement at the most reduced condition (Fsp_9, $Fe^{3+}/Fe_{tot.} = 0.24$) foaming was observed and, consequently, this measurement was discarded.

In order to obtain glass fragments with different $Fe^{3+}/Fe_{tot.}$ ratio necessary for glass transition measurements, the material was sampled after each viscosity measurement using the "dip quench" technique. An alumina-oxide rod was immersed into the melt, withdrawn and plunged into distilled water to ensure a rapid quench. Due to melt sampling and to high volatilization of oxides caused by the high temperature and experimental timescale, fresh glass was used to fill-up the crucible resulting in slightly different bulk compositions for each sample (Table 1). All glasses were verified to be free from crystals by optical, electron microscopy and Raman spectroscopy analyses.

2.2. DSC measurements

The glass transition temperature was measured by differential thermal analysis (DTA) using a differential scanning calorimeter apparatus (DSC 404 Pegasus from Netzsch). The DSC was temperature calibrated with melting standards (indium, bismuth, zinc, aluminium and gold) prior to the test. A sample holder made of platinum was used to perform the measurements under a constant argon flow (quality 5.0, 20 l/min). The furnace atmosphere was set with pure argon with two repeated purging cycles prior to measurement.

Each sample (~30 mg) was heated at 1 °C/min from room temperature up to 100 °C with a dwell time of 30 min to achieve stable conditions. Afterwards, a heating step of 10 °C/min was imposed up to a maximum of 50 °C above the glass transition interval to allow for structural relaxation. Cooling and heating rates of 10 °C/min were imposed in two subsequent thermal treatments to measure the glass transition temperature of the fully relaxed sample. Here, we consider the glass transition temperature peak of the heat flow curve (hereafter defined as T_{gpeak}). Post run optical analysis and Raman spectroscopy measurements performed after each experiment confirmed the absence of thermal alteration and/or oxidation of the samples.

3. Importance of melt structure and Raman spectra deconvolution of natural glasses

The atomic structure of silicate glasses is commonly described in terms of a set of anionic structural units; the so-called "Q^n species". These species are distributed in the structure according to homogeneous equilibria that are directly influenced mainly by the identities of the alkali and alkaline earth elements [23–26].

Q^n species consist of tetrahedral units, typically coordinated by Si^{4+}, Al^{3+} and Fe^{3+} (network-former cations). Q^n species are characterized by a different number (n) of bridging oxygen atoms, which can vary between 0 and 4. This aspect of the melt structure plays a central role in the dynamics of silicate melts [27] and, therefore, on the rheology and relaxation of volcanic melts. Indeed, the relaxation timescale of a melt is controlled by the diffusion of individual atoms (i.e. Q^n species exchange) in the structure [2] with implications for the chemical dependence of the eruptive style of volcanoes [28–30].

Studying Raman spectra may provide insights into the distribution of Q^n species in the structure of glasses and melts [31,32 and references therein]. The region between ~850 and ~1250 cm^{-1} (high wavenumber region, HW) is related to the stretching vibrations of $T{-}O^-$ bonds in different Q^n tetrahedral unit. This region reflects the modification of inter-tetrahedral bond angles, force constants, T—O distances and polymerization due to the action of network modifying and charge balancing cations [24,27,33,34]. Therefore, this part of the Raman spectra is considered in this study.

In order to extract information about the distribution of Q^n species in the structure of our samples, we used a statistical approach to analyze the HW region. A deconvolution method was performed in elementary Gaussian components using the optimization algorithms implemented in the Scientific Python library [35] as reported in Dalou et al. [36]. The band position, intensity and area were treated as independent variables. The code incorporates from statistics science [37] a bootstrap method for the error estimation (see [36] for a detailed discussion).

Table 1
Chemical composition[a] (wt%), iron oxidation state[a], glass transition temperature (T_{gpeak}) and viscosity of the analyzed samples.

Sample	Fsp_1	Fsp_2	Fsp_3	Fsp_4	Fsp_5	Fsp_6	Fsp_7	Fsp_8	Fsp_9
SiO_2	72.53	71.89	72.94	71.93	73.75	73.11	73.44	74.62	74.24
TiO_2	0.44	0.43	0.42	0.43	0.41	0.43	0.43	0.45	0.44
Al_2O_3	8.70	8.78	8.92	8.97	9.06	8.97	9.05	9.05	9.01
Fe_2O_3	8.31	7.24	5.56	6.13	5.91	3.71	3.00	2.05	1.88
FeO[a]	1.54	2.26	3.55	3.42	2.41	5.00	5.01	5.32	5.35
MnO	0.34	0.35	0.37	0.37	0.30	0.37	0.35	0.38	0.36
MgO	0.17	0.16	0.17	0.17	0.15	0.17	0.17	0.18	0.17
CaO	0.45	0.43	0.44	0.46	0.37	0.47	0.40	0.45	0.47
Na_2O	4.59	4.37	4.46	4.72	4.08	4.55	4.08	4.06	4.19
K_2O	4.09	4.01	4.10	4.18	3.94	4.18	3.99	4.05	4.14
Tot.	101.16	99.92	100.93	100.78	100.38	100.96	99.92	100.61	100.25
$Fe^{3+}/Fe_{tot.}$[a]	0.83	0.74	0.58	0.62	0.69	0.40	0.35	0.26	0.24
T_{gpeak} (°C)[b]	–	679.1	673.1	669.3	–	659.9	659.3	–	652.5
log η (Pa s)[c]	3.39	3.34	3.30	3.27	3.21	3.16	3.16	3.22	–

[a] Chemical composition and iron oxidation state measured by EPMA and wet chemistry respectively (from [21]).

[b] Glass transition temperature (peak) measured with a heating/cooling rate of 10 °C/min. For samples Fsp_1, Fsp_5 and Fsp_8 DTA measurements were not performed (see text for details).

[c] Viscosity measured at 1385 °C. Temperature accuracy is ± 1 °C. Viscosities are accurate to ± 0.02 log units based on DGG Standard Glass determinations.