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The equivalence of enthalpy and shear stress relaxation in rhyolitic obsidians and quantification of the liquid–glass transition in volcanic processes

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Abstract

The relaxation of enthalpy and shear stress has been investigated for six silicic volcanic obsidians (calc-alkaline rhyolitic obsidians from Ben Lomond dome, New Zealand, Erevan Dry Fountain, Armenia and Little Glass Butte, USA; peralkaline obsidians from Mayor Island, New Zealand and Eburru, Kenya and a macusanite obsidian from SE Peru). The temperature-dependences of enthalpy and shear stress relaxation are obtained from the dependence of the calorimetric heat capacity peak temperature on heating rate and the dependence of shear viscosity on temperature, respectively. Both processes, enthalpy relaxation and shear stress relaxation, can be approximated to be Arrhenian in the investigated temperature ranges relevant to volcanological processes. Activation energies derived for enthalpy and shear stress relaxation for each sample are equal. This equality permits the calculation of viscosity at the glass transition as a function of cooling rate of a volcanic melt. The relationship between viscosity at the glass transition and the cooling rate is given by $\log_{10}\eta_s(\text{at } T_g) = K - \log_{10}|q|$, where η_s the shear viscosity at the glass transition, q is the cooling rate in °C s^{-1} and K is a constant. The six melt compositions investigated here exhibit a value of $K = 10.49 \pm 0.31$.

For the modeling of volcanic processes, this equation allows the prediction of the viscosity at the glass transition temperature for a given value of cooling rate. Taken together with the Maxwell relation an effective relaxation time can be obtained for the cooling rate. Prediction of the glass transition temperature permits the allotment of temperature ranges for the liquid and glassy segments of the cooling history of the volcanic melt and thus for the correct assignment of glassy and liquid values of the derivative thermodynamic properties, such as expansivity and heat capacity, in thermodynamic modeling of late-stage volcanic processes.

1. Introduction

During eruption, the stress response of all volcanic materials below a critical volume of crystals is controlled by the properties of the melt phase. As a result, the transition in the properties of the melt phase from a liquid-like to a solid-like response in a cooling magma is one of the most fundamental phenomena influencing the emplacement of magma and the eruptive style of volcanic rocks (Dingwell and Webb, 1989, 1990; Dingwell et al., 1993a). The rheological consequences of intersecting this liquid-to-glass or *glass transition* can be catastrophic. A solid-like rheological response implies elastic rather than viscous deformation where the total strain accommodated by elastic deformation is many orders of magnitude less than that accommodated by viscous flow. As a result, sustained stress

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