

Calorimetric glass transition temperatures and magmatic processes

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Glassy rocks have long held a special fascination for petrologists and geochemists because they record the composition of the melt phase attending magmatic processes. Naturally-occurring silicate glasses form under a variety of geological conditions and they commonly form the main constituent in silicic volcanic rocks and in rapidly cooled mafic rocks. Glass also occurs in rocks with cooling histories that are substantially slower, such as the interiors of lava flows or mantle xenoliths. The glass transition temperature (T_g) marks the transition from the liquid to the glassy state. From a petrological perspective, the calorimetrically-defined glass transition temperature is an important limiting value for the temperature conditions at which many magmatic processes take place. Glass formation is a boundary between changing environmental states. Above T_g , rates of nucleation, crystallization and vesiculation are sufficiently fast to drive magmatic processes. Conversely, where the liquid line of descent (e.g., T-X path) intersects the T_g of the melt, glass forms and many magmatic processes effectively cease.

The purpose of this paper is to provide a means of exploring the T-X conditions for glass formation in natural magmatic systems. Specifically, we present an empirical model of predicting the thermodynamic glass transition temperature (T_g) as a function of melt composition. Operationally, the model produces temperature-dependent expressions for the heat contents of a silicate melt and glass of known composition. The point of intersection of the heat content curves for glass and melt defines the calorimetric value of T_g . Our model is constructed from experimental calorimetric heat content and differential scanning calorimetric (DSC) heat capacity measurements on silicate melts and glasses produced over the past 20 years. Calorimetric data in the model include over 500 experiments on 60 melt compositions and 250 observations on 30 glass compositions. Additional constraints on the model derive from independent estimates of the thermodynamic T_g . The model reproduces most of the measured calorimetric-values of T_g to within 30°C. The model also provides volcanologists with a tool for tracking (T_{magma} vs. T_g) through magmatic processes such as fractional crystallization, vesiculation, partial melting. It can be used to forecast the termination of liquid lines of descent by glass formation and provides geothermometric constraints on magmatic systems by converting glass compositions into minimum pre-eruption temperatures.

Thermodynamic models of mantle melting to very high pressure: Molecular dynamics and the macroscopic scale

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In order to characterize melting in the earth's mantle throughout geological time, a thermodynamic model of silicate liquids in the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO-FeO-H}_2\text{O}$ at elevated temperature and pressure in the range 0-135GPa is needed. This is a tall but important task; it represents completion of the agenda NL Bowen set down more than 75 years ago. Because it is unlikely that laboratory-based experimental methods will be able to comprehensively study the relevant portions of P-T-X space, we are using the Molecular Dynamics (MD) method to estimate the structure, thermodynamic and transport properties of multicomponent melts in the mantle system. Although a first-principles MD approach is the most accurate, the computational resources needed to realistically study mantle melting are excessive. We use the simpler approach of empirical two and three body potentials that have been shown to faithfully capture the structure and properties of molten silicates. A key link between the MD (microscopic) and thermodynamic (macroscopic) realms is recognition that profound changes in the short-range order (structure) of molten silicates occur upon increasing pressure. The MD method enables one to capture structural changes systematically and easily in P-T-X space. This information enables development of robust macroscopic entropic 'speciation' models (e.g., mol fraction of SiO_4 , SiO_5 , SiO_6 , etc) and hence development of liquid EOS's. The MD algorithm is explicitly parallel and uses the Particle-Ewald Mesh (PEM) formalism for computation of long-range forces. In addition to the structure, many properties including the internal energy, Helmholtz free energy, isochoric heat capacity, tracer diffusivity of all atoms and the melt shear viscosity can be computed self-consistently. Computed results can be compared to sparse shock wave, phase equilibria and spectroscopic information. Typical results for the compositions MgSiO_3 and Mg_2SiO_4 using available potentials in the equilibrium and metastable liquid field demonstrate the ability of MD methods to provide constraints for macroscopic thermodynamics EOS's. The issue of polyamorphism in the system MgO-SiO_2 is considered as well.