

REVIEWS in MINERALOGY Volume 32

***STRUCTURE, DYNAMICS
AND PROPERTIES OF
SILICATE MELTS***

EDITORS:

J.F. Stebbins, Stanford University

P.F. McMillan, Arizona State University

D.B. Dingwell, Universität Bayreuth

Front cover: Sketch of a possible mechanism for the exchange of silicon species. Oxygens: open circles; network-modifying cations: cross-hatched circles; silicons: solid circles. From Farnan and Stebbins (1994; see Fig.17, p. 222)

Series Editor: Paul H. Ribbe

Department of Geological Sciences

Virginia Polytechnic Institute & State University

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***Structure, Dynamics and Properties
of Silicate Melts***

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STRUCTURE, DYNAMICS AND PROPERTIES OF SILICATE MELTS

FOREWORD

This the thirty-second volume in the *Reviews in Mineralogy* series is the result of contributions from fifteen authors overseen by three editors, Jonathan Stebbins (Stanford), Paul McMillan (Arizona State), and Don Dingwell (Bayreuth), who have worked diligently in selecting the topics and authors and in thoroughly reviewing and cross-referencing the twelve chapters. The result is a definitive treatise on the *Structure, Dynamics and Properties of Silicate Melts*. We apologize that there is rarely time, under the pressure of deadlines and late manuscripts, to assemble an index for most the volumes in this series. But the Table of Contents is detailed, and hopefully the reader will be able to "make do" with this as a means to find his or her way through this vast accumulation of information. There are two other volumes of *Reviews in Mineralogy*, one on *Spectroscopic Methods* (Vol. 18, 1988) and another entitled *Volatiles in Magmas* (Vol. 30, 1994), which are referenced often and are particularly relevant to the subject matter of this book. These are still available at modest cost from the MSA office (address on the opposite page)

The Mineralogical Society of America sponsored a short course for which this was the text at Stanford University December 9 and 10, 1995, preceding the Fall Meeting of the American Geophysical Union and MSA in San Francisco, with about 100 professionals and graduate students in attendance.

I thank Margie Strickler for secretarial help and Jodi and Kevin Rosso for assistance with software problems.

Paul H. Ribbe
Series Editor
Blacksburg, VA

EDITORS' PREFACE

A silicate melt phase is the essential component of nearly all igneous processes, with dramatic consequences for the properties of the Earth's interior. Throughout Earth history and continuing to the present day, silicate melts have acted as transport agents in the chemical and physical differentiation of the Earth into core, mantle and crust. The occurrence of such magmatic processes leads to the definition of our planet as "active," and the resulting volcanism has a profound impact on the Earth's atmosphere, hydrosphere and biosphere. Although near-surface melts are observed directly during volcanic eruptions, the properties of magmas deep within the Earth must be characterized and constrained by laboratory experiments. Many of these experiments are designed to aid in developing an atomic level understanding of the structure and dynamics of silicate melts under the P-T conditions of the Earth's crust and mantle, which will make extrapolation from the laboratory results to the behavior of natural magmas as reliable as possible.

Silicate melts are also the archetypal glass-forming materials. Because of the ready availability of raw materials, and the ease with which molten silicates can be vitrified, commercial "glass" has necessarily implied a silicate composition, over most of the history of glass technology. The properties of the melt, or "slag" in metallurgical extractions, determine the nature of the glass formed, and the needs of the glass industry have provided much of the impetus for understanding the structure-property relations of molten silicates as well as for the glasses themselves. It is now recognized that any liquid might become

glassy, if cooled rapidly enough, and understanding the thermodynamic and kinetic aspects of the glass transition, or passage between the liquid and glassy states of matter, has become a subject of intense interest in fundamental physics and chemistry.

Glasses have also been studied in many geochemical investigations, often as substitutes for the high temperature melts, with the results being extrapolated to the liquid state. In many cases, in situ techniques for direct investigation of these refractory systems have only recently become available. Much valuable information concerning the melt structure has been gleaned from such studies. Nevertheless, there are fundamental differences between the liquid and glassy states. In liquids, the structure becomes progressively more disordered with increasing temperature, which usually gives rise to major changes in all thermodynamic properties and processes. These changes must, in general, be investigated directly by in situ studies at high temperature. Studies of glass only represent a starting point, which reflect a frozen image of the melt "structure" at the glass transition temperature. This is generally hundreds of degrees below the near-liquidus temperatures of greatest interest to petrologists.

Since the early 1980s, a much deeper understanding of the structure, dynamics, and properties of molten silicates has been developed within the geochemical community, applying techniques and concepts developed within glass science, extractive metallurgy and liquid state physics. Some of these developments have far-reaching implications for igneous petrology. The purpose of this Short Course and volume is to introduce the basic concepts of melt physics and relaxation theory as applied to silicate melts, then to describe the current state of experimental and computer simulation techniques for exploring the detailed atomic structure and dynamic processes which occur at high temperature, and finally to consider the relationships between melt structure, thermodynamic properties and rheology within these liquids. These fundamental relations serve to bridge the extrapolation from often highly simplified melt compositions studied in the laboratory to the multicomponent systems found in nature. This volume focuses on the properties of simple model silicate systems, which are usually volatile-free. The behavior of natural magmas has been summarized in a previous Short Course volume (Nicholls and Russell, editors, 1990: *Reviews in Mineralogy*, Vol. 24), and the effect of volatiles on magmatic properties in yet another (Carroll and Holloway, editors, 1994: Vol. 30).

In the chapters by Moynihan, by Webb and Dingwell, and by Richet and Bottinga, the concepts of relaxation and the glass transition are introduced, along with techniques for studying the rheology of silicate liquids, and theories for understanding the transport and relaxation behavior in terms of the structure and thermodynamic properties of the liquid. The chapter by Dingwell presents applications of relaxation-based studies of melts in the characterization of their properties. Chapters by Stebbins, by Brown, Farges and Calas, and by McMillan and Wolf present the principal techniques for studying the melt structure and atomic scale dynamics by a variety of spectroscopic and diffraction methods. Wolf and McMillan summarize our current understanding of the effects of pressure on silicate glass and melt structure. Chapters by Navrotsky and by Hess consider the thermodynamic properties and mixing relations in simple and multicomponent aluminosilicate melts, both from a fundamental structural point of view and empirical chemical models which can be conveniently extrapolated to natural systems. The chapter by Chakraborty describes the diffusivity of chemical species in silicate melts and glasses, and the chapter by Poole, McMillan and Wolf discusses the application of computer simulation methods to understanding the structure and dynamics of molten silicates. The emphasis in this volume is on reviewing the current state of knowledge of the structure, dynamics and physical properties of silicate melts, along with present capabilities for studying the molten state under conditions relevant to melting within the Earth, with the intention that these

techniques and results can then be applied to understanding and modeling both the nature of silicate melts and the role of silicate melts in nature.

This book is the result of the combined efforts of many people to whom we express our heartfelt thanks: the authors themselves; the reviewers who conscientiously gave detailed and useful comments on the chapters, often on extremely short notice; and the Series Editor, Paul H. Ribbe, who made all of this possible with his usual efficiency and aplomb.

Jonathan F. Stebbins
Stanford University, USA

Paul F. McMillan
Arizona State University, USA

Donald B. Dingwell
Universität Bayreuth, Germany

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STRUCTURE, DYNAMICS AND PROPERTIES OF SILICATE MELTS

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Chapter 1

STRUCTURAL RELAXATION AND THE GLASS TRANSITION

Cornelius T. Moynihan

*Materials Science and Engineering Department
Rensselaer Polytechnic Institute
Troy, NY 12180 U.S.A.*

INTRODUCTION: THE NATURE OF STRUCTURAL RELAXATION

In spite of the enormous activity and interest in the subject over the past thirty years or so, the nature of the glass transition and the structural relaxation process in liquids is frequently poorly understood by otherwise knowledgeable scientists or engineers. The purpose of this chapter is to explicate the glass transition, the structural relaxation process and the phenomenology associated therewith in a fairly basic fashion aimed more at fundamental perceptions than at quantitative details. Extensive treatments of much of this material can be found in the books of Brawer (1985), Scherer (1986a) and Nemilov (1995) and in various overview papers (Moynihan et al., 1976; Dingwell and Webb, 1989, 1990; Scherer, 1990; Simmons, 1993; Moynihan, 1994; Hodge, 1994; Angell, 1995).

At the macroscopic thermodynamic level, structural relaxation and the glass transition can be viewed as a phenomenon in which the state of the system depends not only on variables such temperature T , pressure P , shear stress, electric field, etc., but also on what are commonly called order parameters, internal parameters or (in chemistry) progress variables (Moynihan and Gupta, 1978). If one has such a system initially in equilibrium and makes a sudden change in one of the variables (change in T , P , chemical composition, etc.), the system will respond and seek a new equilibrium state consistent with the imposed change. However, the adjustment of the order parameters to new equilibrium values may be kinetically impeded and, in the extreme, be so slow as to be unobservable on any practicable experimental timescale.

Examples of this sort of kinetically impeded adjustment of order parameters to imposed changes abound in our everyday world. Consider, for example, the chemical reaction



where the order parameter describes the relative amounts of reactants and products. At ordinary temperature (25°C) in ordinary Earth atmosphere ($\text{PO}_2 = 0.21 \text{ atm}$, $\text{PCO}_2 = 3.3 \times 10^{-4} \text{ atm}$) the partial pressure of CO at chemical equilibrium is extremely small ($\text{PCO,eq} = 8 \times 10^{-49} \text{ atm}$). If we perturb this system by adding additional CO at ordinary temperature, we might expect most of the added CO to be consumed by reaction with oxygen. This of course will not occur in real time, as demonstrated by the ease with which the CO content in air can rise to and exceed the toxic level ($\text{PCO} = 5 \times 10^{-5} \text{ atm}$). The reaction is too slow at ordinary temperatures. However, this is not the case at higher temperatures, where flammable CO reacts quite readily with O_2 .

Equilibrium constants for chemical reactions are in general temperature dependent. This means that if one starts with a mixture at chemical equilibrium and lowers the temperature, the relative amounts of reactants and products (the order parameter) will also

change, provided that the reaction kinetics are sufficiently rapid. Rates of chemical reactions, however, decrease with decreasing temperature. If one continues to lower the temperature, eventually a point will be reached where the reaction kinetics are unable to keep pace with the imposed temperature changes. Below this temperature regime the chemical composition will remain constant, effectively "frozen" at a value characteristic of equilibrium at a higher temperature. On reheating, the reacting system will re-equilibrate in the same temperature regime in which it initially fell out of equilibrium during prior cooling and subsequently remain in equilibrium when heated to still higher temperatures. An excellent experimental study of this type of phenomenon is to be found in the paper of Barkatt and Angell (1979), in which the chemical reaction was the dimerization of an organic dye in dilute solution in the polyalcohol sorbitol, $C_6H_8(OH)_6$.

There exist other, more "physical" examples of these sorts of order parameter related phenomena. For example, the concentration of vacancies in a metal at equilibrium decreases with decreasing temperature. However, on cooling the vacancy concentration will eventually become "frozen" at a constant value when the rate at which the number of vacancies can decrease by diffusion from the interior of the metal to the surface becomes too slow to keep pace with the temperature change and concomitant shift in the equilibrium vacancy concentration.

The order parameter related phenomenon of interest in this chapter is the change in what is referred to loosely as the "structure" of a liquid or melt in response to temperature (or pressure) changes. In most cases, although we may have a moderately accurate picture of the average structure of a liquid or melt, the changes in that structure that accompany temperature changes are much more subtle and difficult to characterize experimentally. For example, it is universally accepted that the structure of SiO_2 melts and glasses is a disordered, 3-dimensional network of interconnected SiO_4 tetrahedra. Changes in temperature affect some of the detailed features of this disordered network. Best indications, based primarily on infrared and Raman vibrational spectroscopy studies, are that with increasing temperature changes in the average structure of SiO_2 melts are manifested by a decrease in the average Si-O-Si bond angle and an increase in the small number of $(SiO)_3$ siloxane rings in the network (McMillan et al., 1994). As another example, in their study of liquid sorbitol, $C_6H_8(OH)_6$, Barkatt and Angell (1979) found that with decreasing temperature there was a growth in the intensity of an infrared absorption band due to O-H vibrations of -OH groups hydrogen bonded to one another, accompanied by a decrease in the intensity of another band due to non-hydrogen bonded -OH groups. Thus the changes in the "structure" of liquid sorbitol with decreasing temperature are manifested as an increase in the average degree of hydrogen bonding between the molecules.

Rearrangement of the average structure of a liquid is known as *structural relaxation* and has a number of important features:

- (1) Thermodynamic specification of the state of a liquid involves not only specification of T, P, etc., but also of the average structure. That is, like a chemically reacting system or a metal containing vacancies, liquids require an order parameter description.
- (2) Structural relaxation appears to involve breaking and remaking of the bonds between the atoms or molecules, for example, primary Si-O bonds in liquid SiO_2 and intermolecular hydrogen bonds in liquid $C_6H_8(OH)_6$.
- (3) At equilibrium at a given T and P the average structure of a liquid or melt is constant with time. However, this is a dynamic equilibrium, much like a chemically reacting system where at equilibrium the forward and reverse reactions

are occurring at equal rates in opposite directions. At equilibrium in a liquid the local structure is continually rearranging with time, but any changes in one small region are compensated by opposite changes in some other small region, so that the structure averaged over the entire specimen remains constant.

- (4) This continual structural rearrangement is in large part responsible for the fluid character of liquids. Since it involves breaking and remaking of the interatomic or intermolecular bonds, it provides a mechanism whereby atoms or molecules can move past one another during viscous flow or diffusion. For example, diffusion of O^{2-} ions through liquid SiO_2 appears to involve breaking of the Si-O bonds, which is also part and parcel of the structural relaxation process (Dingwell and Webb, 1989, 1990; McMillan et al., 1994).
- (5) Since the structural relaxation process involves breaking and making of bonds, it will contribute to changes in the enthalpy H , entropy S and volume V of a liquid as a function of T and P .
- (6) Just like rates of chemical reactions or vacancy formation in metals, the rate at which structural relaxation occurs decreases with decreasing temperature. At a sufficiently low temperature this rate will become extremely slow, so that the structure of the liquid is "frozen" on an experimental time scale. In this situation the liquid will cease to exhibit fluid behavior and will take on the mechanical and thermodynamic properties of a solid. When this occurs we no longer refer to the amorphous system as a *liquid*. Rather, we refer to it as a *glass*.

PHENOMENOLOGY OF STRUCTURAL RELAXATION

Isothermal relaxation

Experimentally the most straightforward way to detect the structural relaxation process is to carry out observations in a temperature range where structural relaxation is very slow compared to the timescale over which properties of the liquid can be determined. One allows the liquid to equilibrate on this experimental time scale, subjects the specimen to a rapid change in temperature (or pressure), and then follows the evolution with time of some experimentally measurable macroscopic property (enthalpy H , volume V , refractive index n) at the new temperature (or pressure). The results of such an experiment are shown schematically in Figure 1 for the evolution of H or V of a melt initially in equilibrium after a step change in temperature from T_1 to T_2 imposed at time $t = 0$. The melt initially exhibits a "fast" or glass-like change in H or V associated primarily with the vibrational degrees of freedom. This is followed by a "slow" or kinetically impeded further change in H or V associated with the structural relaxation process. Structural relaxation progresses until equilibrium is reached at the new temperature. At the top of Figure 1 the molecular events attending these two processes are conceptualized for a network oxide liquid. In the fast or glass-like process there is a decrease in the amplitude of the atomic vibrations, very similar to what would occur in the corresponding crystal if the temperature were decreased. This leads to a net decrease in the distance of separation of the atoms, but no change in their relative positions. In the subsequent slow structural relaxation there is a change in the liquid structure involving breaking and remaking of bonds, suggested in Figure 1 as a decrease in the average ring size.

Results of experiments of this sort are frequently described in terms of changes in the fictive temperature, T_f . T_f is defined as the contribution of the structural relaxation process to the property of interest (H or V in Fig. 1) expressed in temperature units and may be considered as a measure of the order parameter associated with the structural relaxation process. For the equilibrium liquid, $T_f = T$, and during heating or cooling $dT_f/dT = 1$. For

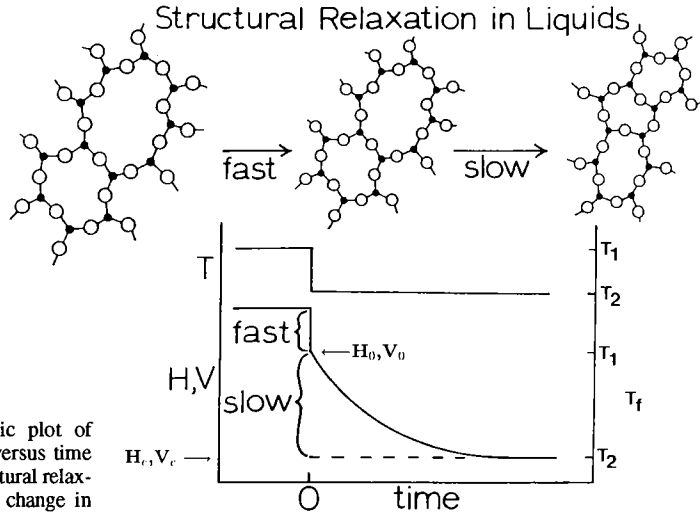


Figure 1. Schematic plot of enthalpy and volume versus time during isothermal structural relaxation following a step change in temperature.

a glass whose structure is frozen, $T_f = \text{constant}$, and during heating or cooling $dT_f/dT = 0$. As shown in Figure 1, during the course of structural relaxation following a step change in temperature from T_1 to T_2 , T_f varies from T_1 to T_2 in parallel with the changes in H or V . It should be emphasized that T_f is not a quantity of fundamental significance, but is merely an auxiliary variable defined for computational and conceptual convenience. Moreover, the value of T_f is not necessarily a unique or complete specification of the structural state frozen into a glass. For example, T_f values calculated from different properties (e.g. H and V) for a glass formed by rate cooling will in general be slightly different.

The rate of structural relaxation may be described by a characteristic structural relaxation time, τ . As a crude first approximation, we might assume that the rate of approach of, say, enthalpy H to equilibrium in the experiment of Figure 1 will be proportional to the deviation of H from the equilibrium value H_e approached at long times at temperature T_2 :

$$d(H - H_e)/dt = -k(H - H_e) \quad (2)$$

where k is a rate constant. Integrating this expression between time 0 and time t we get:

$$\phi(t) \equiv \frac{H - H_e}{H_0 - H_e} \equiv \frac{T_f - T_2}{T_1 - T_2} = \exp(-kt) \equiv \exp\left(-\frac{t}{\tau}\right) \quad (3)$$

where $\phi(t)$ is called the relaxation function and varies from 1 at $t = 0$ to 0 at very long times, H_0 is the enthalpy at time $t = 0$ immediately following the fast glass-like response of the liquid, and the structural relaxation time τ is defined as the inverse of the rate constant ($\tau = 1/k$). For small departures from equilibrium and over a short temperature range the temperature dependence of τ can be approximated by an Arrhenius expression:

$$\tau = \tau_0 \exp(\Delta H^*/RT) \quad (4)$$

where τ_0 is a pre-exponential constant, ΔH^* an activation enthalpy, and R is the ideal gas constant. Because ΔH^* is positive, τ increases and the rate of structural relaxation decreases rapidly with decreasing temperature.

Relaxation during cooling and heating

Cooling or heating a liquid or glass at a rate $q = dT/dt$ can be thought of as a series of small temperature steps ΔT followed by isothermal holds of duration $\Delta t = \Delta T/q$. In Figure 2a is shown the behavior of the enthalpy H of a glassforming liquid during stepwise cooling followed by stepwise reheating over the same temperature range. [Volume V and other properties would behave similarly.] The dashed line represents both the temperature T and the equilibrium enthalpy H_e . The solid line represents the experimentally measured enthalpy H . Following the first downward step in temperature, the relaxation time τ is sufficiently short compared to the time interval Δt ($\Delta t \gg \tau$) that the system is able to equilibrate and exhibits a liquid-like response for the enthalpy. Following the second downward step, however, the relaxation time is now longer at the lower temperature, and the system is unable to equilibrate completely ($\Delta t \sim \tau$). The extent of equilibration in time Δt becomes less and less after each subsequent downward temperature step, so that after the last two such steps virtually no structural relaxation occurs in time interval Δt ($\Delta t \ll \tau$), the system exhibits only the fast glass-like change in H (compare Fig. 1), and the relaxational part of the enthalpy is frozen at a value much greater than the equilibrium value. At this point the system is behaving as a glass.

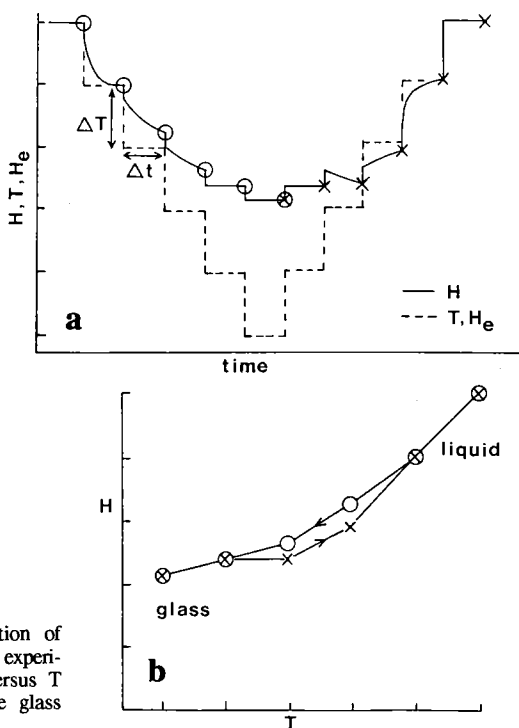


Figure 2. Schematic plots of (a) variation of temperature T , equilibrium enthalpy H_e , and experimental enthalpy H with time, and (b) H versus T during stepwise cooling and reheating in the glass transition region.

Following the first upward step in temperature during reheating in Figure 2a, the relaxation time τ is still too long to allow structural relaxation in time interval Δt . Hence the enthalpy exhibits only the fast glass-like change, but now in an upward direction. Following the second upward step the system can exhibit partial relaxation. Since, however, H is above the equilibrium value at this point, it exhibits a downward relaxation,

even though the system is now being heated. Following the third and subsequent upward temperature steps, H is below the equilibrium value H_e . Hence it now relaxes upwards and is eventually able to equilibrate in time Δt at the highest temperatures, so that the system has returned to liquid-like behavior.

The enthalpy H at the beginning and end of each time/temperature step in Figure 2a is plotted versus temperature in Figure 2b. The intermediate temperature region over which the system passes from liquid-like behavior to glass-like behavior and in which $\Delta t \sim \tau$ is called the *glass transition* region. Note that in the glass transition region the H vs. T cooling curve is different from the H vs. T heating curve, so that there is hysteresis between the two curves when a liquid is cooled and subsequently reheated through the transition region. This hysteresis is in no way unique to structural relaxation in liquids and the glass transition. Rather it is expected for any chemical or physical process requiring an order parameter description (e.g., a chemical reaction or disappearance and formation of vacancies in a metal crystal) when the equilibrium state of the system and the rate of approach to equilibrium are both temperature dependent. Note also that the glass transition, as explicated here, is entirely kinetic in origin and is not to be confused with thermodynamic transitions, such as melting of a crystal or vaporization of a liquid, which can take place at equilibrium.

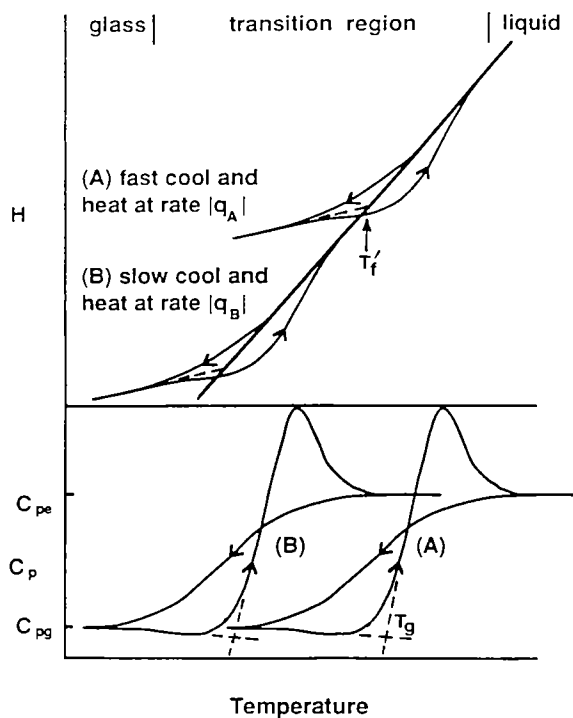


Figure 3. Schematic plots of enthalpy H and heat capacity C_p versus temperature during cooling and reheating through the glass transition region at two different rates.

Shown schematically in the upper part of Figure 3 are plots of H vs. T similar to that in Figure 2b for cooling and reheating through the glass transition region at two different rates, q_A and q_B ($q_A > q_B$) (Moynihan et al., 1974; Moynihan, 1994). During cooling the H vs. T plot changes slope monotonically as one passes from liquid to glass through the glass transition region. If instead of monitoring H directly one monitored the heat capacity C_p

(= dH/dT = slope of H vs. T curve), as is commonly done using differential scanning calorimetry (DSC) or differential thermal analysis (DTA), one would obtain the sigmoidal C_p vs. T cooling curves shown in the lower part of Figure 3. Because of the hysteresis between the H vs. T curves during cooling and reheating, the slope of the H vs. T curve on reheating passes through a maximum near the upper end of the glass transition region. This leads in turn to maxima in the C_p vs. T reheating curves, as shown in the lower part of Figure 3. Note that these maxima in the C_p reheating curves, which are often taken to be an essential or definitive feature of the glass transition, are in fact an artifact of fairly straight-forward kinetics for the structural relaxation process coupled with a continual shift in the parameters characterizing the rate of the process (e.g., k or τ in Eqns. 2 and 3) and in the departure of the system from equilibrium due to the continually changing temperature.

Although the glass transition covers a finite range in temperature, this range is fairly narrow and is commonly demarcated by a glass transition temperature T_g . T_g may be taken as any characteristic point on the cooling or reheating curve for a measured property or the temperature derivative of that property. If, for example, the property is enthalpy H , T_g might be taken as the extrapolated onset of rapid increase of the C_p vs. T reheating curve, as shown in the bottom part of Figure 3. Alternatively, T_g might be taken as the extrapolated point of intersection, denoted T_f' in the upper part of Figure 3, of the liquid and glass H vs. T curves measured during cooling. [T_f' as defined in Figure 3 is the limiting fictive temperature attained by cooling the liquid to well below the glass transition region.]

Shown in Figure 4 are plots of C_p (= dH/dT) and of the temperature derivative of the volume dV/dT of a $\text{Na}_2\text{Si}_2\text{O}_5$ glass vs. T measured during rate heating through the glass transition region at $5^\circ\text{C}/\text{min}$ after prior cooling at $5^\circ\text{C}/\text{min}$ (Webb, 1992). Both heating curves exhibit the shapes expected from the lower part of Figure 3 (rapid rise followed by a maximum in C_p and dV/dT) and serve to demarcate the glass transition region. Also worth

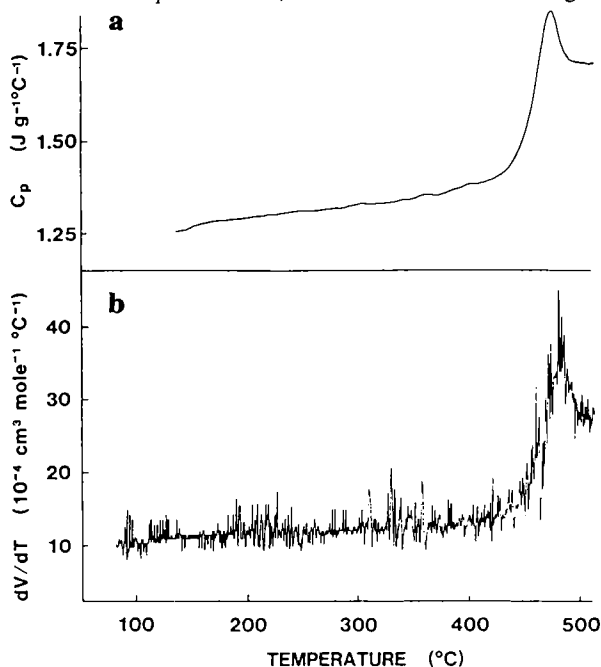


Figure 4. Heat capacity C_p and temperature derivative of volume dV/dT of $\text{Na}_2\text{Si}_2\text{O}_5$ glass during reheating at $5\text{ K}/\text{min}$ after prior cooling at $5\text{ K}/\text{min}$ through the glass transition region (Webb, 1992).

noting in Figure 4 is the close agreement between the C_p and dV/dT curves in terms of, for example, the temperatures and relative heights of the maxima. This suggests that the kinetics of the structural relaxation process monitored in terms of enthalpy H are very similar to those monitored in terms of volume V for silicate melts (Knoche et al., 1992). This correlation, however, is neither expected nor found experimentally to hold true for all types of glassforming liquids (Moynihan and Gupta, 1978).

Dependence of T_g on cooling and heating rate

As discussed above, during cooling and subsequent reheating the glass transition is observed in a temperature regime where the characteristic time scale $\Delta t = \Delta T/q$ becomes comparable to the structural relaxation time τ . Since a change in the cooling or heating rate q alters this time scale, it follows that the relaxation time τ in the glass transition region will be similarly altered. Since τ in turn is temperature dependent (cf. Eqn. 4), it then follows that a change in cooling or heating rate will change the location (temperaturewise) of the glass transition region and the value of T_g . In particular, as shown schematically in Figure 3, increasing the cooling or heating rate will shift the transition region to higher temperatures and increase the measured value of T_g . This is illustrated in Figure 5, which shows DSC traces for heating of As_2Se_3 glass through the glass transition at three different rates after cooling through the transition region at the same respective rates (Moynihan et al., 1974). The DSC output is proportional to the heat capacity C_p . Aside from some distortion of the DSC curves at low heating rates due to baseline curvature, the three DSC curves agree with the schematic curves in Figure 3. The glass transition temperatures, which might be taken from any characteristic points on the curves such as T_{g1} , T_{g2} or T_{g3} , shift uniformly upward in temperature with increasing heating rate.

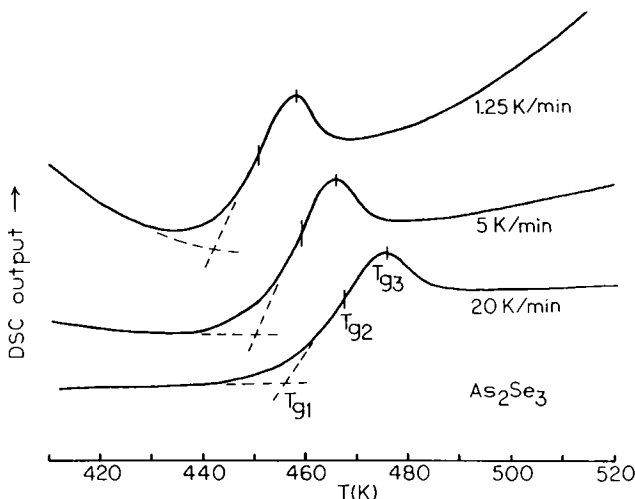


Figure 5. Differential scanning calorimeter traces for reheating of As_2Se_3 glass through the glass transition region at various rates after cooling through the transition region at the same respective rates.

It can be shown (Moynihan et al., 1974) that experiments of the type in Figures 3 and 5 (reheating rate proportional to cooling rate) can be used to obtain the activation enthalpy ΔH^* of Equation (4), which specifies the temperature dependence of the structural relaxation time in the transition region:

$$d \ln q_r / d(1/T_g) = -\Delta H^* / R \quad (5)$$

where q_h is the heating rate. If one defines the glass transition temperature as the limiting fictive temperature T_f' attained on cooling through the transition region, one can analogously obtain ΔH^* from the dependence of T_f' on cooling rate q_c (Moynihan et al., 1976):

$$d \ln |q_c| / d(1/T_f') = -\Delta H^* / R \quad (6)$$

(These last two expressions remain valid even when the nonlinear and nonexponential features of structural relaxation described in a subsequent section are taken into account.) Note that, since the glass and equilibrium liquid property vs. T curves are the same for cooling and subsequent reheating, T_f' may be determined from the reheating curves. Any reheating rate may be used for this determination and will presumably be chosen to optimize experimental accuracy and precision. If, as in a DSC experiment, the property monitored is enthalpy H and the instrumental output is proportional to the temperature derivative of the property ($C_p = dH/dT$), determination of the extrapolated intersection of the glass and equilibrium H vs. T curves corresponds to a matching of areas under the measured C_p vs. T plots. Determination of T_f' in this fashion is illustrated in Figure 6 for a B_2O_3 glass reheated at 10 K/min after being previously cooled through the glass transition region at 10 K/min. The equation governing the area match is

$$\int_{T \gg T_g}^{T_f'} (C_{Pe} - C_{Pg}) dT = \int_{T \gg T_g}^{T \ll T_g} (C_P - C_{Pg}) dT \quad (7)$$

where C_{Pg} is the glass heat capacity observed below the transition region and C_{Pe} is the equilibrium liquid heat capacity observed above the transition region. Shaded area I in Figure 6 corresponds to the left side of this expression and shaded area II to the right side. Note from Figure 6 that, when the prior cooling and reheating rates are the same, T_f' obtained from the C_p reheating curve is very close to T_g in Figure 3 or T_{g1} in Figure 5 defined as the extrapolated onset of rapid rise of the C_p vs. T reheating curve.

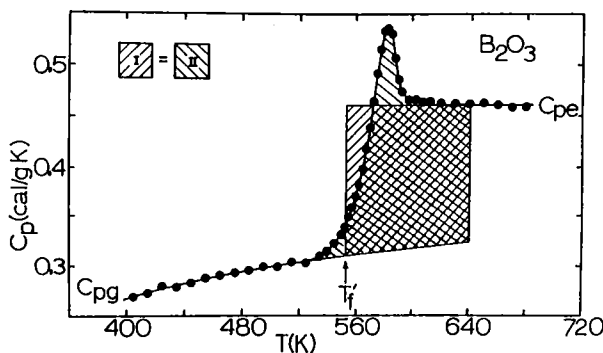


Figure 6. Heat capacity versus temperature for B_2O_3 glass during heating at 10 K/min following a rate cool at 10 K/min through the glass transition region. T_f' is the limiting fictive temperature attained by the glass on cooling at 10 K/min.

In Figure 7 is shown an Arrhenius plot of $\log |q_c|$ vs. $10^3/T_f'$ (K) for an As_2Se_3 glass (Easteal et al., 1977). The T_f' values were obtained from C_p vs. T curves during reheating at 10 K/min after prior cooling through the transition region at rates ranging from -0.31 to -20 K/min. The slope of the plot gives via Equation (6) an activation enthalpy ΔH^* of 342 kJ/mol for structural relaxation of As_2Se_3 glass in the glass transition region. This is a large activation enthalpy, so that although the cooling rate has been varied by a factor of 65 ($= 20/0.31$) in the experiments of Figure 7, the glass transition temperature as measured by T_f' has only changed by about 20 K (from 435 K to 455 K). Note from Equation (4) that this also means that the characteristic structural relaxation time τ also decreases by a factor of 65 between 435 K and 455 K.

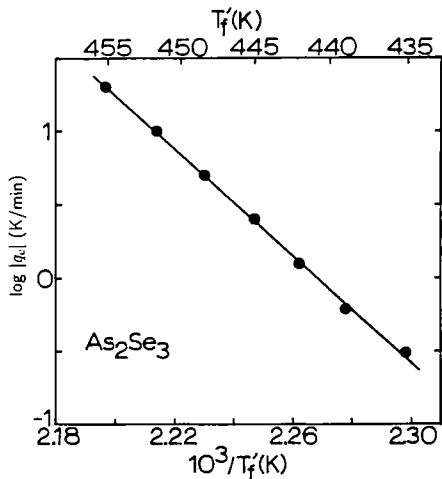


Figure 7. Logarithm of cooling rate $|q_c|$ versus reciprocal of limiting fictive temperature for As_2Se_3 glass.

KINETICS OF STRUCTURAL RELAXATION

Isothermal relaxation

Although the simple first order kinetic expressions of Equations (2) and (3) give an accurate qualitative description of the progress of the structural relaxation process with time following a step change in temperature from equilibrium, they fail to give an acceptable quantitative description. A quantitative description requires that two additional features be taken into account. The first of these is the *nonlinear* character of the process (in the sense that the rate of relaxation cannot be described by a linear differential equation such as Eqn. 2). This is illustrated in Figure 8 for the isothermal relaxation of the density ($\propto 1/V$) of a soda lime silicate glass (Scherer, 1986b). In the upper curve the glass was initially equilibrated at 500°C (so that its initial fictive temperature $T_f = 500^\circ\text{C}$), then upquenched to 530°C and allowed to relax at that temperature. In the lower curve the glass was initially equilibrated at 565°C (initial $T_f = 565^\circ\text{C}$), then downquenched to and allowed to relax at 530°C . At long times both samples have come to equilibrium (final $T_f = \text{annealing temperature} = 530^\circ\text{C}$) and exhibit the same density. [The densities in Figure 8 were actually measured at room temperature after dropping the samples out of the furnace following annealing for various times at 530°C . Hence the fast, glass-like contribution to the density change (cf. Fig. 1) has effectively been subtracted from all the data points.] Even though

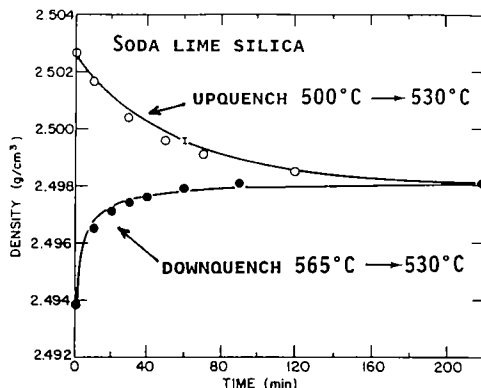


Figure 8. Isothermal relaxation at 530°C of the density of a soda lime silicate glass following an upward step change in temperature from 500°C (upper curve) and a downward step in temperature from 565°C (lower curve). Solid lines are calculated from Equations (8), (14) and (15) using the parameters $\tau_0 = 3.9 \times 10^{-37}$ s, $\Delta H^* = 607$ kJ/mol, $x = 0.45$ and $\beta = 0.62$.

the initial magnitude of departure of the density from equilibrium is nearly the same for both specimens and even though they are relaxing at the same temperature (530°C), the downquenched sample with the higher initial T_f (= 565°C) clearly relaxes more quickly than the upquenched sample with the lower initial T_f (= 500°C). In terms of Equations (3) and (4) this means that the structural relaxation time τ depends not only on temperature T but also on the instantaneous structure or fictive temperature. One common way of modifying Equation (4) to account for this is to use the so-called Tool-Narayanaswamy (TN) equation:

$$\tau = \tau_0 \exp\left[\frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f}\right] \quad (8)$$

where x ($0 \leq x \leq 1$) is the nonlinearity parameter. Note that Equations (4) and (8) become identical in the limit of small departures from equilibrium ($T_f \rightarrow T$).

Another way of accounting for the nonlinearity is via the Adam-Gibbs equation (Scherer, 1984; Hodge, 1994; Richet and Bottinga, this volume):

$$\tau = \tau_0 \exp\left[\frac{B}{TS_c(T_f)}\right] \quad (9)$$

where B is a constant and the configurational entropy $S_c(T_f)$ is presumed to be a function of the fictive temperature:

$$S_c(T_f) = \Delta C_p \ln(T/T_K) \quad (10)$$

ΔC_p ($= C_{p_l} - C_{p_g}$) is the difference between the liquid and glass heat capacities, and T_K is the temperature at which the configurational entropy of the liquid would vanish at equilibrium. Over a short temperature range for moderate departures from equilibrium Equations (8) and (9) cannot be distinguished functionally from one another (Scherer 1986; Hodge, 1994).

The second of the aforementioned features of the structural relaxation process is its *nonexponential* character. This means that even for relaxation very close to equilibrium where $T_f \approx T$ and nonlinear effects are unimportant, isothermal relaxation cannot be described by the simple exponential function of Equation (3). To account for this feature a distribution of relaxation times is incorporated into the relaxation function

$$\phi(t) = \sum_i g_i \exp\left[-\int_0^t dt' / \tau_i\right] \quad (11)$$

where the g_i are temperature independent weighting coefficients ($\sum_i g_i = 1$) for the contributions from the various relaxation times τ_i . Each τ_i is given by an expression of the form of Equation (8):

$$\tau_i = \tau_{i0} \exp\left[\frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f}\right] \quad (12)$$

or of Equation (9)

$$\tau_i = \tau_{i0} \exp\left[\frac{B}{TS_c(T_f)}\right] \quad (13)$$

Hence the τ_i differ only in their pre-exponential factors τ_{i0} . This, along with the presumed temperature independence of the g_i , leads to a condition known as thermorheological simplicity. The need for an integral over time in Equation (11) is due to the variation of T_f and hence of the τ_i with time during relaxation.

The microscopic interpretation of a distribution of relaxation times in the relaxation function of Equation (11) remains something of an open question. To return for a moment

to the chemical reaction analogy to the structural relaxation process, imagine a system in which two or more independent chemical reactions could take place. If one monitored the evolution of the enthalpy or volume of such a system as it equilibrated isothermally, one would expect nonexponential behavior, since each reaction would make an independent contribution to the changes in H and V with time, but it would be very unlikely that the rate constants k_i or relaxation times τ_i for the different reactions would be the same. This suggests in turn that during structural relaxation in liquids there may be a number of different molecular events involved which occur at different rates. Alternatively, some microscopic regions of the liquid may differ from other microscopic regions, so that the various regions relax at different rates. These differences might arise from thermally generated differences (fluctuations) in the configurational entropy S_c from microregion to microregion, which would lead via Equation (9) to differences in the local relaxation times (Moynihan and Schroeder, 1993).

The number of adjustable parameters in Equations (11) and (12) or (13) may be considerably reduced if one selects a continuous distribution or spectrum of relaxation times, the shape of which can be specified by a single parameter and the location of which on a logarithmic timescale can be specified by a reference relaxation time τ (e.g. the most probable relaxation time). One then need worry only about the T and T_f dependence of the reference relaxation time τ , which is presumed to be of the form of Equation (8) or (9). A common choice for the shape of the spectrum of relaxation times, which seems to give a good fit to most data, is that corresponding to the so-called Kohlrausch-Williams-Watts (KWW) or stretched exponential relaxation function:

$$\phi(t) = \exp\left[-\left(\int_0^t dt'/\tau\right)^\beta\right] \quad (14)$$

where β ($0 < \beta \leq 1$) is the nonexponentiality parameter. Hence, to describe structural relaxation in response to temperature changes for substantial departures from equilibrium one requires a minimum of four adjustable parameters. In Equations (8) and (14) these are τ_0 , ΔH^* , x and β . [For most glasses a "substantial departure from equilibrium" means a difference between T_f and T greater than about 2 K.] The solid lines in Figure 8 are fits to the data using Equations (8) and (14), where the relaxation function for density ρ and the fictive temperature T_f is defined by (compare Fig. 1 and Eqn. 3):

$$\phi(t) = \frac{\rho(t) - \rho_e}{\rho_0 - \rho_e} = \frac{T_f(t) - T_2}{T_1 - T_2} \quad (15)$$

Relaxation during cooling and heating

Structural relaxation in response to a complicated thermal history, e.g., a temperature change ΔT_1 at time t_1 , ΔT_2 at time t_2 , ..., ΔT_m at time t_m , may be dealt with by using the Boltzmann superposition principle in conjunction with Equations (8) or (9) and (14). Here we assume that the total response of the system is just the sum of its responses to each of one of the temperature steps starting at the time that temperature step is imposed. In this situation the fictive temperature $T_f(t)$ at time t ($t > t_m$) is given by

$$T_f(t) = T_0 + \sum_{j=1}^m \Delta T_j [1 - \phi(t, t_j)] \quad (16)$$

where T_0 is an initial temperature at which the sample is at equilibrium, and

$$\phi(t, t_j) = \exp\left[-\left(\int_0^{t-t_j} dt'/\tau\right)^\beta\right] \quad (17)$$

An example of such a complicated thermal history is cooling at rate q_c from a temperature T_0 above the glass transition region to well below the transition region and then

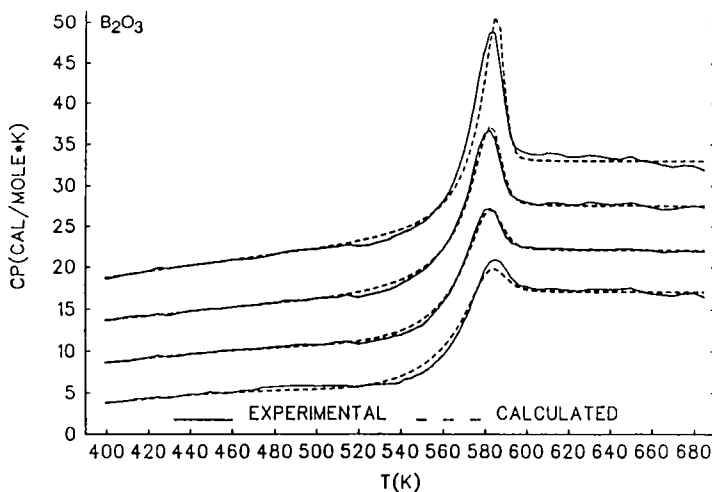


Figure 9. Heat capacities of B_2O_3 glass measured during heating at 10 K/min after cooling through the transition region at rates of 0.62, 2.5, 10 and 40 K/min (top curve to bottom curve). Heat capacity scale is correct for top curve; other curves have been displaced downward for clarity. Solid lines are experimental data. Dashed lines are calculated from Equations (8), (16), (17) and (18) using the parameters $\tau_0 = 1.3 \times 10^{-33}$ s, $\Delta H^* = 377$ kJ/mol, $x = 0.39$ and $\beta = 0.62$.

reheating at a (possibly different) rate q_h to above the transition region, as schematically shown in Figures 2 and 3. In Figure 9 are shown some actual data of this sort for B_2O_3 glass, where the solid lines are plots of the heat capacity C_p measured by DSC during rate heating at 10 K/min following cooling through the transition region at a variety of rates ranging from -0.62 to -40 K/min (DeBolt et al., 1976; Moynihan et al., 1991). The dashed lines were obtained from a fit to the C_p heating data using Equations (8), (16) and (17) and the τ_0 , ΔH^* , x and β parameters given in the figure caption. T_0 in Equation (16) was taken as a temperature well above the transition region ($T_0 = 630$ K) where the relaxation time τ is short enough that the liquid remains in equilibrium during the cooling and heating rates employed. Equation (16) was used to calculate T_f and dT_f/dT during the initial cool through the transition region, followed by the subsequent reheat. C_p was then obtained from the expression (compare Eqn. 7):

$$dT_f/dT = (C_p - C_{pg})/(C_{pe} - C_{pg}) \quad (18)$$

As might be expected, changes in prior thermal history (cooling rate in the case of Fig. 9) affect the subsequent relaxational behavior of the system (during reheating in the case of Fig. 9). In Figure 9 this is manifested mainly as an increase in the maximum in C_p during reheating at the same rate with decreasing prior cooling rate. This in turn reflects via Equation (6) the decrease in T_f' with decreasing cooling rate and the effect of this via Equation (8) on the relaxational kinetics during subsequent reheating. More drastic changes in the prior thermal history can have even more pronounced effects on the relaxational behavior during subsequent reheating (Moynihan, 1994). This is illustrated in Figure 10 for a ZBLA glass, where prolonged sub-T_g annealing causes a substantial upward shift in the temperature region for structural relaxation and in the value of T_g measured during reheating at a given rate.

The calculated density and C_p curves in Figures 8 and 9 agree with the measured curves within experimental error. This is generally found to be the case when the departure

from equilibrium during actual relaxation is not extremely large. When this condition is not met, e.g. during annealing of a glass at temperatures very far below T_g , the quantitative agreement between the experimental data and best fits using Equations (8), (9), (14), (16) and (17) deteriorates to varying degrees, but all of the qualitative features of the experimental data are accurately reproduced in the calculated curves (Scherer, 1986; Gupta and Huang, 1992; Ducroux et al., 1994). It thus seems fair to conclude that the structural relaxation process and the glass transition are well understood from a macroscopic, phenomenological standpoint.

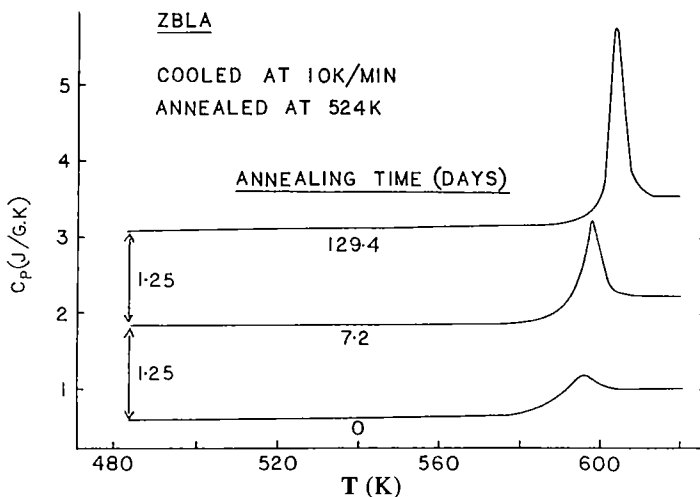


Figure 10. Heat capacities of $58\text{-ZrF}_4\text{-}33\text{-BaF}_2\text{-}5\text{-LaF}_3\text{-}4\text{-AlF}_3$ (ZBLA) glass measured during heating at 10 K/min after cooling through the transition region at 10 K/min and sub- T_g annealing at 524 K for times shown in the figure. Heat capacity scale is correct for the bottom curve. Other curves have been displaced upwards for clarity.

CORRELATIONS BETWEEN STRUCTURAL RELAXATION AND SHEAR VISCOSITY

Listed in Table 1 are structural relaxation and shear viscosity data in the glass transition region for a variety of inorganic glasses with T_g well above room temperature. These are mostly network oxide glasses, but examples of non-oxide glasses (As_2Se_3 and ZBLA) are also included. The data were compiled from a number of sources (Napolitano and Macedo, 1968; Tauber and Arndt, 1987; Knoche et al., 1992; Dingwell et al., 1993; Moynihan, 1993, 1994; Moynihan et al., 1995). T_g is the glass transition temperature defined as in Figure 3 and measured by DSC during heating at 10 K/min after cooling at a comparable rate. [Values of T_g for the glasses in Table 1 were actually measured at a variety of heating rates ranging from 5 to 20 K/min, but have been corrected where necessary to a standard heating rate of 10 K/min using Equation (5).] In the third column of Table 1 are listed values of $\log\langle\tau\rangle$, the logarithm of the mean or average equilibrium structural relaxation time at T_g determined from analysis of C_p data as in Figure 9. This mean relaxation time in terms of Equations (11) or (14) is defined respectively by

$$\langle\tau\rangle = \sum_i g_i \tau_i \quad \text{or} \quad (\tau/\beta)\Gamma(1/\beta) \quad (19)$$

where Γ signifies the gamma function. By "equilibrium" relaxation time we mean that this

is the value of $\langle\tau\rangle$ corresponding to $T = T_g = T_g$ in Equations (8), (9), (12) or (13).

Table 1. Glass transition temperatures T_g measured by DSC at 10 K/min heating rate, logarithms of mean equilibrium enthalpy structural relaxation times $\langle\tau\rangle$ and shear viscosities η at T_g , and activation enthalpies ΔH^* and ΔH_η^* for structural relaxation and viscous flow in the glass transition region.

Glass	$T_g(K)$	$\log\langle\tau\rangle(s)$	$\log\eta(Pa\cdot s)$	ΔH^* (kJ/mol)	ΔH_η^* (kJ/mol)
As ₂ Se ₃	454	2.4	10.8	342	322
B ₂ O ₃	557	2.6	11.4	385	385
ZBLA	587	2.8	11.6	1400	1140
lead silicate (NBS 711)	714	2.6	11.9	374	411
0.25Na ₂ O-0.75SiO ₂	748	2.7	11.6	410	435
GeO ₂	810	—	11.5	—	303
alkali lime silicate (NBS 710)	832	2.6	11.8	612	612
alkali borosilicate (BSC)	836	—	12.1	615	615
diopside (CaMgSi ₂ O ₆)	973	—	12.7	—	965
anorthite (CaAl ₂ Si ₂ O ₈)	1109	—	12.6	—	1084

As noted earlier, during cooling or reheating the glass transition region occurs in the temperature range where there is approximate correspondence between the time scale of the experiment and the characteristic relaxation time ($\Delta t \sim \tau$). For rate-cooling and -heating experiments this time scale is set by the cooling and heating rates q_c and q_h . Consequently, it is to be expected that the value of $\langle\tau\rangle$ at T_g observed at comparable prior cooling and reheating rates should be virtually the same for all glasses, as is borne out by the data in Table 1. For reheating at 10 K/min after cooling at a comparable rate, $\langle\tau\rangle$ at T_g is approximately $10^{2.6} s = 400 s$. This is in line with the frequently made assertion that the characteristic relaxation time at T_g is of the order of $10^2 s$.

Also listed in Table 1 are the logarithms of the shear viscosities η at T_g , along with the structural relaxation activation enthalpies ΔH^* (obtained as in Fig. 7) and the corresponding shear viscosity activation enthalpies ΔH_η^* in the glass transition region, where

$$d \ln \eta / d(1/T) = \Delta H_\eta^* / R \quad (20)$$

As suggested in the initial section of this chapter, the microscopic mechanism by which structural relaxation occurs should be intimately connected with the mechanism of viscous flow under a mechanical stress. The data in Table 1 bear this out. The shear viscosities at T_g of these inorganic glasses are all very similar and lie in the range typically 10^{11} to 10^{12} Pa s. Indeed, the temperature at which $\eta = 10^{12}$ Pa s is often used as an indicator of T_g .

Likewise, the activation enthalpies ΔH^* and ΔH_η^* which characterize the temperature dependences of the structural relaxation time and the shear viscosity appear to be identical within experimental error.

Over an extended temperature range Arrhenius plots of $\log \eta$ vs. $1/T$ for glassforming melts commonly exhibit curvature or non-Arrhenius behavior to varying degrees. A good method, popularized by Angell (Angell, 1991 and 1995), of comparing this non-Arrhenius viscosity behavior for various melts is to plot $\log \eta$ vs. a normalized reciprocal temperature T_g/T , where T_g is taken as the temperature where $\eta = 10^{12}$ Pa s. An example of such a plot is shown in Figure 11 (Lee et al., 1993). Melts such as SiO_2 whose $\log \eta$ vs. T_g/T plots are nearly linear have been termed "strong" liquids by Angell, in the sense that they retain their high viscosities over a large range as the temperature increases relative to T_g . At the other extreme are melts such as ZBLA, whose viscosities exhibit a highly non-Arrhenius temperature dependence and decrease rapidly to very fluid values as the temperature rises above T_g ; these are termed "fragile" liquids.

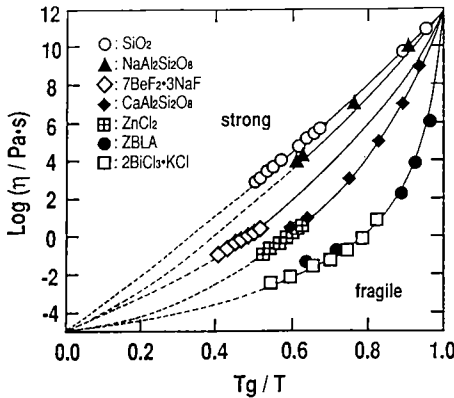


Figure 11. Plots of the logarithms of the shear viscosities of several melts versus normalized inverse temperature T_g/T .

In terms of the viscosity activation enthalpies defined in Equation (20), the slopes of the plots in Figure 11 are given by

$$d \log \eta / d(T_g/T) = \Delta H_\eta^* / 2.3RT_g \quad (21)$$

Moreover, as pointed out by Angell, the $\log \eta$ vs. T_g/T curve for a particular liquid in Figure 11 is determined by its slope $\Delta H_\eta^* / 2.3RT_g$ at T_g . Hence strong liquids exhibit an Arrhenius viscosity temperature dependence and have low values of $\Delta H_\eta^* / T_g$ at T_g . Fragile liquids exhibit a highly non-Arrhenius temperature dependence and a large value of $\Delta H_\eta^* / T_g$ at T_g .

The reason why some melts show an Arrhenius and others a non-Arrhenius viscosity temperature dependence over a long range in temperature and viscosity can be explicated using the Adam-Gibbs theory, as originally pointed out in a paper on the viscosity of the strong liquid BeF_2 (Moynihan and Cantor, 1968). The Adam-Gibbs expression (cf. Richet and Bottinga, this volume, and Eqns. 9 and 10) for the shear viscosity of an equilibrium melt ($T_f = T$) above T_g is given by

$$\eta = \eta_0 \exp\left[\frac{B_\eta}{TS_c(T)}\right] = \eta_0 \exp\left[\frac{B_\eta}{T\Delta C_P \ln(T/T_K)}\right] \quad (22)$$

where η_0 and B_η are constants. The melt viscosity will be roughly Arrhenius and the $\log \eta$ vs. $1/T$ plot roughly linear if the temperature dependence of the configurational entropy

$S_c(T)$ and hence the value of ΔC_p are small. A highly temperature dependent $S_c(T)$ and a large value of ΔC_p will give highly non-Arrhenius behavior. Hence in Angell's terms strong liquids have small ΔC_p values and fragile liquids have large ΔC_p values, a correlation that appears to be quite well borne out experimentally when comparing liquids of the same general type (e.g. comparing network oxide melts) (Angell, 1991 and 1995). Since the fragility of a liquid also corresponds to a large value of $\Delta H_\eta^*/T_g$ at T_g , one also expects a positive correlation between ΔC_p and $\Delta H_\eta^*/T_g$ at T_g . Such a correlation has been demonstrated very clearly in a recent series of papers by Minami and coworkers (Lee et al., 1993, 1994 and 1995) and is exemplified in Figure 12.

The heat capacity difference ΔC_p between liquid and glass is a measure of the contribution of the structural changes in the liquid to the enthalpy H as a function of temperature, the evolution of which with time is monitored in structural relaxation experiments. Hence a strong liquid with a small ΔC_p has a structure which maintains its "integrity" fairly well as the temperature increases above T_g , while a fragile liquid with a large ΔC_p has a structure which "falls apart" rapidly with increasing temperature.

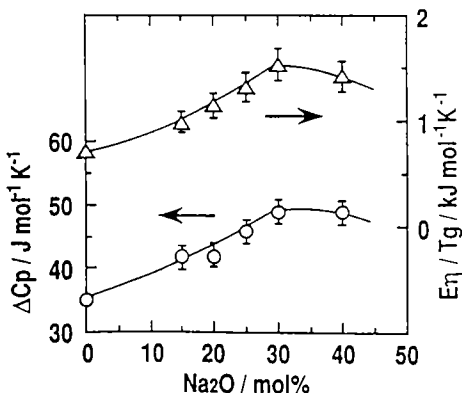


Figure 12. Composition dependences of ΔC_p and H_η^*/T_g ($= E_\eta/T_g$) at T_g for $x\text{-Na}_2\text{O}-(100-x)\text{-B}_2\text{O}_3$ melts (Lee et al., 1995).

CONCLUSIONS

The glass transition, as explicated here, appears to be a strictly kinetic phenomenon and can be described in much the same way as the kinetics of chemical reactions are described. Presently unanswered or only partly answered questions with regard to the glass transition are of two (not unrelated) types. The first has to do with the nature of the structural relaxation process itself, that is, how the equilibrium structures of liquids change with changing temperature and pressure and what detailed molecular mechanisms are involved in the structural rearrangement. There are obviously no completely generic answers to these questions; each different liquid will have its own unique structure and mode of structural rearrangement. Obtaining detailed answers for specific liquids will depend, among other things, upon improvements in the precision and accuracy of spectroscopic and diffraction characterization and computer simulation of melt structures and dynamics. The second type of question has to do with the kinetic expressions used to describe the structural relaxation process, the physical reasons behind the nonlinear and nonexponential relaxational behavior, and the proper way to model structural relaxation occurring very far from equilibrium where the treatments described in this chapter are no longer quantitatively adequate.

On a more positive note, there has been sizeable progress in the past thirty years in our perception of and ability to model the detailed behavior of melts in the glass transition

region. Some of these advances remain to be exploited. For example, as seen in Figures 9 and 10, the behavior of glasses on reheating through the transition region are strongly dependent on their previous thermal history, e.g. prior cooling rate and annealing time and temperature. This means that one should be able to infer this previous history from reheating experiments. Obvious candidates for such studies are naturally occurring geological glasses.

REFERENCES

- Angell CA (1991) Relaxation in liquids, polymers and plastic crystals—strong/fragile patterns and problems. *J Non-Cryst Solids* 131-133:13-31
- Angell CA (1995) Formation of glasses from liquids and biopolymers. *Science* 267:1924-1935
- Barkatt A, Angell CA (1979) Optical probe studies of relaxation processes in viscous liquids. *J Chem Phys* 70:901-911
- Brawer S (1985) Relaxation in Viscous Liquids and Glasses. American Ceramic Soc, Columbus, OH
- DeBolt MA, Eastale AJ, Macedo PB, Moynihan CT (1976) Analysis of structural relaxation using rate heating data. *J Am Ceram Soc* 59:16-21
- Dingwell DB, Webb SL (1989) Structural relaxation in silicate melts and non-newtonian melt rheology in geologic processes. *Phys Chem Minerals* 16:508-516
- Dingwell DB (1990) Relaxation in silicate melts. *Eur J Mineral* 2:427-449
- Dingwell DB, Knoche R, Webb SL (1993) A volume temperature relationship for liquid GeO_2 and some geophysically relevant derived parameters for network liquids. *Phys Chem Minerals* 19:445-453
- Ducroux J-P, Rekhson SM, Merat FL (1994) Structural relaxation in thermorheologically complex materials. *J Non-Cryst Solids* 172-174:541-553
- Eastale AJ, Wilder JA, Mohr RK, Moynihan CT (1977) Heat capacity and structural relaxation of enthalpy in As_2Se_3 glass. *J Am Ceram Soc* 60:134-138
- Gupta PK, Huang J (1992) Enthalpy relaxation in glass fibers. In: *The Physics of Non-Crystalline Solids*. Pye LD, LaCourse WC, Stevens HJ (eds) Taylor and Francis, Washington, DC, p 321-326
- Hodge IM (1994) Enthalpy relaxation and recovery in amorphous materials. *J Non-Cryst Solids* 169:211-266
- Knoche R, Dingwell DB, Webb SL (1992) Temperature-dependent thermal expansivities of silicate melts: the system anorthite-diopside. *Geochim Cosmochim Acta* 56:689-699
- Lee S-K, Tatsumisago M, Minami T (1993) Transformation range viscosity and thermal properties of sodium silicate glasses. *J Ceram Soc Japan* 101:1018-1020
- Lee S-K, Tatsumisago M, Minami T (1994) Fragility of liquids in the system $\text{Li}_2\text{O}-\text{TeO}_2$. *Phys Chem Glasses* 35:226-228
- Lee S-K, Tatsumisago M, Minami T (1995) Relationship between average coordination number and fragility of sodium borate glasses. *J Ceram Soc Japan* 103:398-400
- McMillan PF, Poe BT, Gillet Ph, Reynard B (1994) A study of SiO_2 glass and supercooled liquid to 1950 K via high temperature Raman spectroscopy. *Geochim Cosmochim Acta* 58:3653-3664
- Moynihan CT, Cantor S (1968) Viscosity and its temperature dependence in molten BeF_2 . *J Chem Phys* 48:115-119
- Moynihan CT, Eastale AJ, Wilder J, Tucker J (1974) Dependence of the glass transition temperature on heating and cooling rate. *J Phys Chem* 78:2673-2677
- Moynihan CT, Eastale AJ, DeBolt MA, Tucker J (1976) Dependence of fictive temperature of glass on cooling rate. *J Am Ceram Soc* 59:12-16
- Moynihan CT et al (1976) Structural relaxation in vitreous materials. *Ann NY Acad Sci* 279:15-35
- Moynihan CT, Gupta PK (1978) The order parameter model for structural relaxation. *J Non-Cryst Solids* 29:143-158
- Moynihan CT, Crichton SN, Opalka SM (1991) Linear and non-linear structural relaxation. *J Non-Cryst Solids* 131/133:420-434
- Moynihan CT, Schroeder J (1993) Non-exponential structural relaxation, anomalous light scattering and nanoscale inhomogeneities in glass-forming liquids. *J Non-Cryst Solids* 160:52-59
- Moynihan CT (1993) Correlation between the width of the glass transition region and the temperature dependence of the viscosity of high-Tg glasses. *J Am Ceram Soc* 76:1081-1087
- Moynihan CT (1994) Phenomenology of the structural relaxation process and the glass transition. In: *Assignment of the Glass Transition*, Seyler RJ (ed) ASTM STP 1249, ASTM, Philadelphia, PA, p 32-49
- Moynihan CT, Lee S-K, Tatsumisago M, Minami T (1995) Estimation of activation energies for structural relaxation and viscous flow from DTA and DSC experiments. *Thermochim Acta*, in press
- Napolitano A, Macedo PB (1968) Spectrum of relaxation times in GeO_2 glass. *J Res NBS* 72A:425-433

- Nemilov SV (1995) *Thermodynamic and Kinetic Aspects of the Vitreous State*, CRC Press, Ann Arbor, MI
- Richet P, Bottinga Y, Rheology and configurational entropy of silicate melts. This volume
- Scherer GW (1984) Use of the Adam-Gibbs equation in the analysis of structural relaxation. *J Am Ceram Soc* 67:504-511
- Scherer GW (1986a) *Relaxation in Glass and Composites*, Wiley-Interscience, New York
- Scherer GW (1986b) Volume relaxation far from equilibrium. *J Am Ceram Soc* 69:374-381
- Scherer GW (1990) Theories of relaxation. *J Non-Cryst Solids* 123:75-89
- Simmons JH (1993) Viscous flow and relaxation processes in glass. In: *Experimental Techniques in Glass Science*, Simmons CJ, El-Bayoumi OH (eds) Am Ceram Soc, Westerville, OH, p 383-432
- Tauber P, Arndt J (1987) The relationship between viscosity and temperature in the system anorthite-diopside. *Chem Geol* 62:71-81
- Webb SL (1992) Shear, volume, enthalpy and structural relaxation in silicate melts. *Chem Geol* 96:449-457

Chapter 2

RELAXATION IN SILICATE MELTS: SOME APPLICATIONS

D. B. Dingwell

*Bayerisches Geoinstitut
Universität Bayreuth
95440 Bayreuth, Germany*

INTRODUCTION

In the past decade a significant body of research has been generated in the geosciences that has referred to relaxation in silicate melts. Consideration of the relaxation timescale has provided criteria for the clear distinction between equilibrium and nonequilibrium behavior of silicate melts, led to the identification and correction of errors in previous studies of the structure and properties of silicate melts, and inspired new experiments to measure melt properties. Yet the treatments of the concepts of structural or property relaxation in molten silicates that have emerged in recent years are not, as a rule, new. Many are to be found in contributions to the fields of physical chemistry of liquids and properties of glass melts. The enhanced recognition of the potential applications of relaxation-based studies of silicate melts in the fields of geochemistry and petrology/volcanology in the past decade serve at least two purposes. First, relaxation-based studies have enhanced our ability to quantify the P-V-T equation of state, thermodynamic and transport properties of geo-relevant melts improving our ability to estimate magma properties that serve as vital parameters in igneous processes. Second, the range of melt compositions covered by igneous processes describes an otherwise poorly-investigated area of melt physics and chemistry. By uncovering the behavior, for example, of highly silicic, water-rich, tectosilicate melts, we are able to build up structure-property relationships for melts that are not only of great theoretical importance for models of geological melt behavior but also contribute in a significant way to the general description of liquids in the physical sciences.

This chapter is concerned with some recently developed applications of the nature of relaxation in silicate melts in the description of bulk melt properties. Further discussion of the relaxational aspects of certain property determinations are covered in the chapters by Richet and Bottinga and by Webb and Dingwell in this volume. Discussions of relaxational aspects of spectroscopic and computer simulation studies are also included in the chapters by McMillan and Wolf, by Stebbins and by Poole et al. A discussion of the relationship of the glass transition to diffusion processes is in the chapter by Chakraborty. Recent advances in the area of interaction timescales for multiphase systems (not covered here) have recently been reviewed by Dingwell et al. (1993a). The emphasis here is on the contribution that relaxation studies have made to the development of new experimental pathways to the description of melt properties and melt behavior during magmatic processes.

FUNDAMENTALS

Phenomenology and significance of the glass transition

One of the most fundamental aspects of the physical properties of silicate melts is that they can exhibit both liquid-like and solid-like behavior. We denote solid-like behavior in amorphous materials as glassy and the transition from liquid-like behavior to glassy

behavior as the glass transition. Virtually all melt properties are affected by the glass transition. Some properties, such as viscosity and shear modulus are drastically affected. Thus a description of the nature of the glass transition is an important first step towards the description of silicate melts themselves.

The glass transition has been traditionally defined in terms of its phenomenology as "that phenomenon... in which a solid amorphous phase exhibits with changing temperature a more or less sudden change in the derivative thermodynamic properties such as heat capacity and thermal expansivity from crystal-like to liquid-like values." (Wong and Angell, 1976). This behavior is illustrated schematically in Figure 1. The curve labeled p records the value of a melt property, P , measured during cooling of a silicate melt at a constant rate. Two segments of the curve are apparent. The inflection point is termed the glass transition of the sample material and the temperature at which the inflection occurs is the glass transition temperature recorded by the experiment (T_g). The temperature-dependent value of p at temperatures above T_g corresponds to liquid-like behavior. The temperature-dependent value of p at temperatures below T_g is solid-like or glassy behavior. If we record the temperature dependence of property p at a differing cooling rates and concentrate on the behavior in the vicinity of the inflection point of Figure 1a then we observe the behavior illustrated in Figure 1b; a path dependent hysteresis in the variation of the derivative properties in the glass transition interval.

The location of the inflection point shifts to higher values of temperature with increasing cooling rate and to lower values of temperature with decreasing cooling rate. This behavior can be used to describe a relationship between cooling rate and inflection or glass transition temperature. Such a relationship is illustrated in Figure 2. Intuitively, it can be appreciated that a slower cooling rate provides more time for the structure and properties of the silicate melt to relax to temperature-induced changes during cooling. We will see below that this can be quantified, but first we need to introduce the concept of a relaxation time.

If a silicate melt is subjected to an instantaneous change (i.e. step function) of an intensive thermodynamic variable such as temperature, the resulting change in the structure and extensive properties of the liquid is not an instantaneous one. Instead, the structure and properties of the melt "relax" towards the new equilibrium values of the thermodynamic properties as a function of time. The time taken to accomplish this re-equilibration is the relaxation time. The cooling ramp, implicit in Figure 1b, can be considered to be a series of

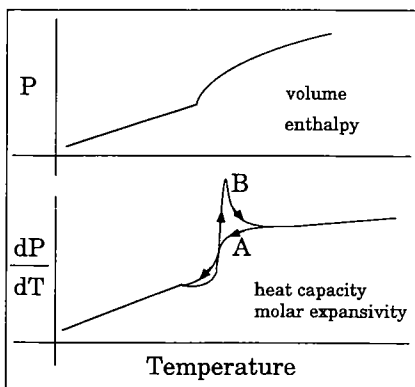


Figure 1. A schematic illustration of the variation of an arbitrary melt property, P (e.g. volume, enthalpy) and the temperature derivative of the property, dP/dT (e.g. expansivity, heat capacity) as a function of temperature. The temperature dependence of the melt property is divided by the glass transition temperature into a low temperature segment formed from the locus of values for the glassy state and a high temperature segment formed from the locus of values for the liquid state. The derivative properties illustrate (in an expanded temperature scale) that the glass transition is a region of finite width in which transient values of the derivative properties are recorded during heating and cooling transects. These transient values of the properties are path dependent and influenced by the kinetic material parameters, the temperature scanning rate and direction and (for the case of heating) the thermal history of the glass.

small steps in temperature separated by short isothermal time intervals during which the sample can approach or relax to the new equilibrium values of its properties. A log unit change in the cooling rate can be approximated by a log unit change in these isothermal time intervals and thus in the time available for the relaxation process during cooling. The relationship between relaxation time and cooling rate is thus seen to be a linear one. The trace of T_g versus time, in Figure 2, illustrates a fundamental point concerning the transition from liquid to glass. The glass transition is a curve in temperature-time space which divides the dynamic behavior of silicate melts into two fields of response; a liquid field at long timescales and high temperatures and a solid-like or glass field at short timescales and low temperatures. In Figure 2 these relations are generalized into a plot of time versus (reciprocal absolute) temperature. All processes concerning the dynamic response of silicate melts can be plotted in Figure 2 given knowledge of their characteristic timescales or rates and of their temperatures. Such processes include all experiments designed to measure the properties or structure of silicate melts and all petrogenetic processes involved in the formation of igneous rocks. Our description of the temperature dependence of silicate melt properties below will be repeatedly placed in the reference frame provided by Figure 2.

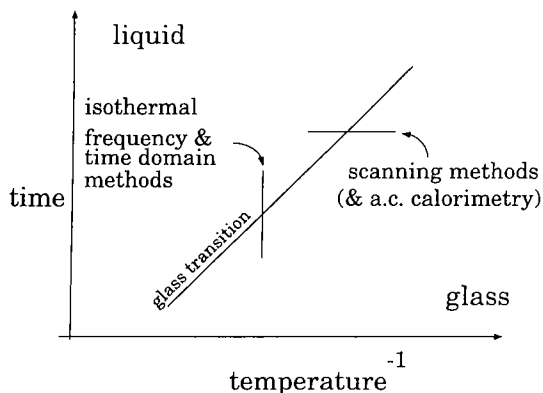


Figure 2. A schematic representation of the glass transition in reciprocal temperature-time space. The relationship between timescale of observation and resulting transition temperature yields an "activation energy" for relaxation processes. The glass transition may be investigated by (1) transects in which the timescale of the investigation is variable (e.g. time and frequency domain methods) and the relaxation of the melt to a state of equilibrium following a perturbation of the system is measured isothermally or by (2) transects in which the timescale of the observations is held constant and the temperature is scanned such that the temperature dependence of the melt properties and structure are the source of the perturbation from equilibrium. Both types of experiments yield comparable quantification of the relaxation time in silicate melts.

As noted above, the glass transition can be phenomenologically defined as the temperature where the properties of the melt change from those of the liquid-like state to those of the solid-like state (Wong and Angell, 1976; Dingwell and Webb, 1989; 1990). This is perhaps best pictured as a rheological glass transition between a dominantly viscous and a purely elastic response of the melt to an applied stress; that is, a transition between viscous dissipation and elastic storage of strain energy. Using the example of shear deformation, which, in the case of sustained, externally applied, stress also yields the brittle-ductile transition with its catastrophic consequences for volcanism, the timescale of the transition can be approximated via the Maxwell relationship for shear:

$$\tau = \frac{\eta_N}{G_\infty} \quad (1)$$

where η_N is the relaxed Newtonian shear viscosity, G_∞ is the unrelaxed elastic shear modulus and τ is the relaxation time. In this sense the shear viscosity and shear modulus can be thought of as energy *loss* and *storage moduli*, respectively. The shear viscosity is exponentially dependent on temperature and the shear modulus is essentially independent of temperature and composition and can be usefully approximated for this purpose to be a constant 10 GPa (Dingwell and Webb, 1990). The relaxation time is therefore represented by a time-temperature curve for each melt composition. The temperature dependence of the Maxwell relaxation time for any silicate melt can be readily approximated from the measured viscosity-temperature relationship together with either a measured or estimated value for the shear modulus to within a factor of two. Thus the resulting curves look very similar to the viscosity-temperature relationships of these melts. Normally, the viscosities of multicomponent melts can be calculated to within a similar uncertainty at superliquidus temperatures. Thus the shear relaxation time of melts of geological interest can be estimated for the relatively high temperatures and low viscosities relevant to eruptive temperatures.

Unfortunately, in this regard, the relationship between cooling rate and relaxation time presented below illustrates that the relaxation times corresponding to the glass transition in natural processes, and in most experiments, are much longer than those corresponding to the high temperatures and low viscosities mentioned above. Viscosity data in the range of 10^9 to 10^{15} Pa s, relatively high viscosities for experimental determination, are those that are needed in order to predict the shear relaxation time and, in combination with cooling rate data, the glass transition temperature for natural processes and for experimental quenching. The determination of viscosities in this range is possible with a number of methods (Dingwell, 1995) but most of them are more time consuming than high temperature, concentric cylinder viscometry. For this and other reasons, such as the metastability of most if not all silicate melts in this viscosity range, relatively few data are presently available, although this area is receiving considerable attention at present (see chapter by Richet and Bottinga). The shear relaxation time, derived from the Maxwell relation with the assumption of a temperature-independent G_∞ , is plotted in Figure 3 for several examples of melts for which relatively complete viscosity-temperature relationships exist. The non-Arrhenian temperature dependence of these curves is the reason why low range viscosity data cannot be used, in general, to extrapolate the estimation of shear relaxation time to lower temperatures. Figure 3 illustrates well the range of relaxation time that is exhibited by silicate melts due to their temperature dependence and their composition dependence of viscosity. In this calculation, the temperature dependence of viscosity contributes to a variation in shear relaxation time of up to 12 orders of magnitude between the glass transition temperature of industrial processes and the practical onset of liquid instability due to melt volatilisation. The composition dependence of the viscosity leads to a variation in the "classical" glass transition temperature (that defined by industrial glassmaking processes), from approximately 1300°C for very pure SiO_2 to approximately 450°C for alkali silicates. In Figure 4 recent data for what is probably the most intensely investigated silicate glassforming system, $\text{Na}_2\text{O-SiO}_2$, are presented (Knoche et al., 1994). The greatest variation in glass transition temperature is accomplished with minor contamination of SiO_2 by water or alkalis leading to a drop of over 800°C with the addition of a few mole % of Na_2O (Fig. 5). The exact functional form of the decrease of T_g with composition near SiO_2 is not very well known and yet the sheer magnitude of the effect makes its explanation one of the challenges to all theories of relaxation.

The pressure dependence of the glass transition is very poorly known. The measurements are difficult to perform. Differential thermal analysis measurements offer an opportunity for high pressure measurements yet only one study has been conducted. Data for albite, diopside and sodium trisilicate glasses are reproduced from the study of Rosenhauer et al. (1979) in Figure 6 for pressures up to 7 kbar. The variation in glass transition temperature is very minor and positive for diopside and sodium trisilicate but

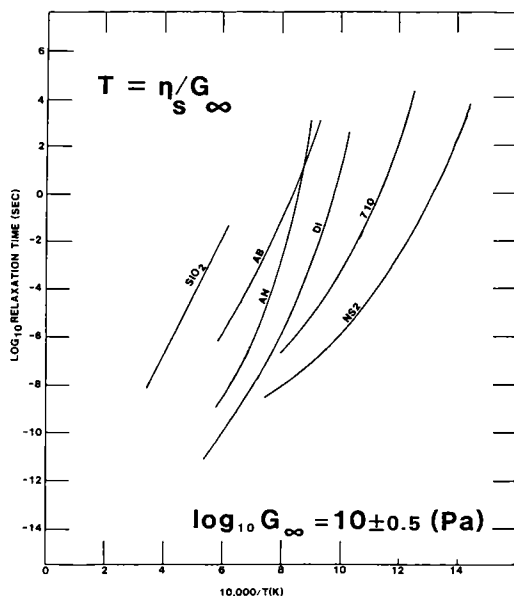
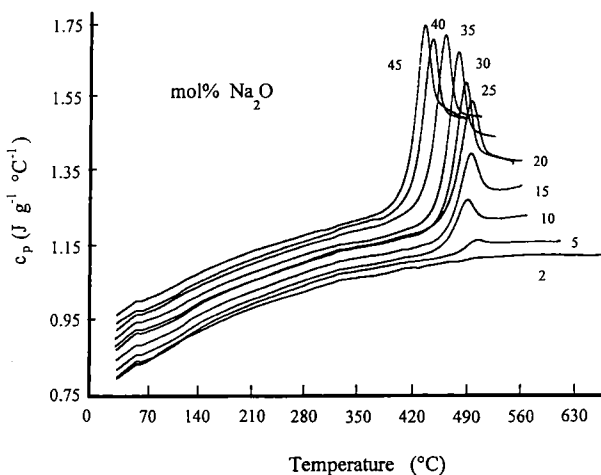


Figure 3. Quantification of the relaxation time-temperature relationship for several silicate melts through the use of shear viscosity data and the approximation of a constant value of the shear modulus together with the Maxwell relation. (AB = albite, AN = anorthite, DI = diopside, 710 = NBS SRM 710 soda lime glass, NS2 = Na-disilicate). For sources of viscosity data see Dingwell and Webb (1990 from whom this figure is reproduced).

negative for albite. These data, combined with evidence for a significant decrease in the high temperature viscosity of silicic melts from falling sphere investigations (Kushiro, 1978a,b; Dingwell, 1987) lead to the inference of greater melt fragility at higher pressure.

Figure 4. Variation in character and temperature of the glass transition in the $\text{Na}_2\text{O}-\text{SiO}_2$ system determined using scanning calorimetry. Note that the signal of the glass transition becomes almost immeasurably small with increasing SiO_2 . Comparison of these data with estimates of the glass transition of pure SiO_2 reveal a catastrophic drop of the glass transition with the addition of a few percent of alkali oxide to the base composition. Variation of T_g with composition in the high SiO_2 range is complex and is a primary challenge to theories of relaxation in silicate melts. Reproduced with permission from Knoche et al. (1994).



Experimental timescales and relaxation times

All experimental investigations of the properties and structure of silicate melts have timescales associated with them. The timescales are imposed by different types of experiments in different ways. Experiments that employ sinusoidal oscillations of an extrinsic field have a frequency which can be inverted to obtain a timescale. Such frequency-domain experiments are powerful probes of the structure and properties of silicate melts because the frequency, and thus the timescale, of the experimental probe can be varied over several log units to study the frequency-dependence of certain melt properties. Examples of such experiments designed to measure physical properties are the

methods of ultrasonic wave propagation, specific heat spectrometric, a.c. conductivity and torsion pendulum studies. Similarly, stress-strain experiments sample melt properties on timescales that can be calculated as the inverse of the strain rate during sample deformation. Examples include constant strain-rate or constant stress determinations of viscosity, such as concentric-cylinder and fiber elongation, respectively.

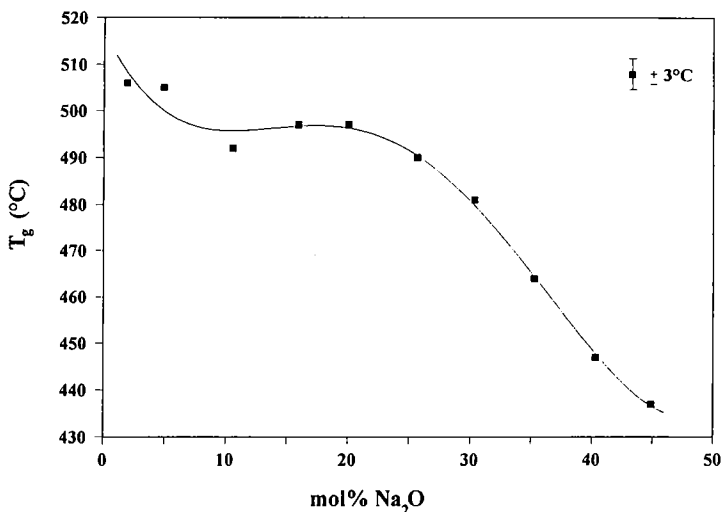


Figure 5. Variation in the glass transition temperature of melts in the system $\text{Na}_2\text{O}-\text{SiO}_2$. The T_g of SiO_2 lies well above 1000°C . In contrast, the total variation in T_g from 20 to 45% Na_2O is a mere 60°C . Reproduced with permission from Knoche et al. (1994).

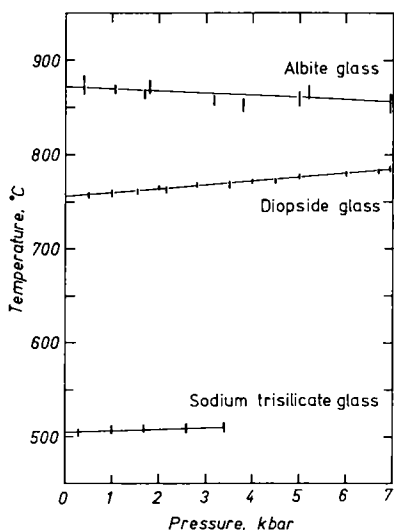


Figure 6. The variation of the glass transition temperature of silicate melts of albite, diopside and sodium trisilicate composition from 1 bar to 7 kbar determined using differential thermal analysis. The variations in this pressure range are slight. Comparison with available data on the higher temperature viscosities of albite melt at similar pressures indicates a decrease in activation energy at low viscosity which can only be reconciled with the relative invariance of T_g with pressure (pictured here) if albite melt becomes more fragile with increasing pressure. Reproduced with permission from Rosenhauer et al. (1979).

Experiments that employ a temperature scan, such as scanning calorimetric or dilatometric methods, operate on timescales that can be calculated from a comparison of stress relaxation times with the temperature dependence of the inflection in properties

marking the glass transition. Each cooling/heating rate corresponds to a defined relaxation timescale for the experiment (quantified below).

With knowledge of the timescale of the experimental probe, the location of a particular experiment with respect to the relaxation timescale of the silicate liquid can be determined. Depending on the temperature and timescale either relaxed liquid or unrelaxed glassy melt properties will be recorded by the experiment. Most experiments are confined to certain distinct ranges of temperature (and pressure). In addition each experimental set-up is constrained in terms of the magnitude and dynamic range over which data can be acquired. Thus the absolute temperature and the temperature dependence of the melt properties themselves control the range of temperature over which property measurements can be made using a given technique. A compilation of experimental and relaxation timescales is provided in Figure 7.

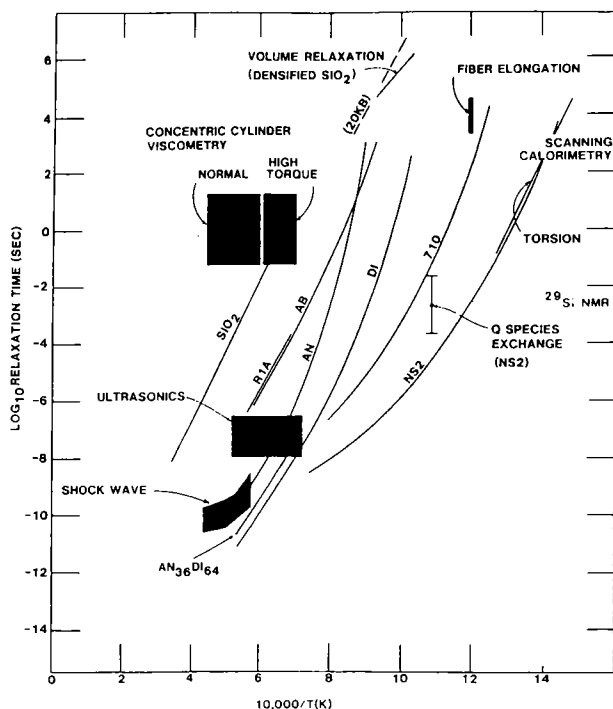


Figure 7. Comparison of the timescales commonly accessed by several experimental methods for the study of melt properties compared with the relaxation times calculated as in Figure 3 for several melt compositions. The sources of experimental timescales are discussed in Dingwell and Webb (1989). Reproduced from Dingwell and Webb (1989).

Volume versus enthalpy relaxation

Volume and enthalpy record significant inflections in their temperature dependence at the glass transition. The temperature dependence of volume and enthalpy and their derivative properties, expansivity and heat capacity, was illustrated schematically in Figure 1. The temperature dependence can be divided into a low temperature segment reflecting the glassy or solid-state properties of the melts, a high temperature segment corresponding to the liquid state properties of the melt and an intermediate temperature region of complex property variations across the glass transition. As we will see below actual calorimetric and dilatometric data for the heat capacity and expansivity of silicate melts respectively differ in the magnitudes of their temperature dependence and of their behavior in the glass transition

interval. Nevertheless, to a very good approximation, the glass transition temperatures derived from both types of scanning experiments yield the same glass transition temperatures as, for example read from the peak temperatures of the derivative property curves. This is briefly illustrated in Figure 8a,b where heat capacity and expansivity data together with a normalization of the heat capacity and expansivity scans of a sample (in this case a 50:50 anorthite:diopside composition melt) with identical cooling history and heating rate has been performed such that the glassy temperature-dependent heat capacity equals 0 and the peak maximum equals 1. This normalization serves to correct out the differences in *magnitude* of variations of the two properties, heat capacity and expansivity, which are distinct for most melts, from the *relative* variations in the transient values of those properties in the glass transition interval, which are determined solely by the temperature-dependent *kinetic* properties of the sample and the experiment. The tight overlap of the normalized heat capacity and expansivity curves up to the peak temperature (where viscous deformation invalidates the expansivity trace) indicates that the peak position, the form and thus the underlying kinetics controlling the relaxation of both enthalpy and volume are very similar and possibly identical. This equivalence of volume and enthalpy relaxation provides a simplification which serves below as a powerful tool for the investigation of melt and magma properties.

The equivalence of relaxation behavior and timescale for such disparate properties as enthalpy and volume begs the question of whether the shear stress relaxation time is also equivalent to that of volume and enthalpy relaxation.

Volume versus shear relaxation

The determination of volume relaxation times for silicate melts may be directly carried out by annealing samples of glass and serially measuring their densities following perturbation of the system by a pressure or a temperature step (e.g. Ritland, 1954; Höfler and Seifert, 1984). Relatively few such data exist. An alternative approach, for which relatively many data exist, is the ultrasonic determination of sound velocities and attenuation from which viscosity may be determined. From the identity relating volume, shear and longitudinal moduli of isotropic substances,

$$M = K + (4/3)G \quad (2)$$

we can write a viscous equivalent

$$\eta_L = \eta_v + (4/3)\eta_s \quad (3)$$

where η_L , η_v , and η_s are the longitudinal, volume and shear viscosities, respectively.

Compendia of the elastic constants of silicate glasses (e.g. Bansal and Doremus, 1986) indicate that the shear (or rigidity) modulus and the bulk modulus of silicate glasses are similar in magnitude. Studies of the propagation of longitudinal ultrasonic waves in a small number of natural silicate melts (Sato and Manghnani, 1984) have also demonstrated that concentric-cylinder data and (ultrasonic) longitudinal wave attenuation data yield shear and longitudinal viscosity data that are also similar in magnitude. Dingwell and Webb (1989) later demonstrated that the extensive longitudinal wave attenuation data set of Rivers and Carmichael (1987) was consistent with the proposal that the volume and shear viscosities of the investigated melts were equal. Figure 9 illustrates this comparison using literature data for shear viscosities (see Dingwell and Webb, 1989, for data sources), the longitudinal viscosity data noted above, and Equation (3), to obtain volume viscosity by difference.

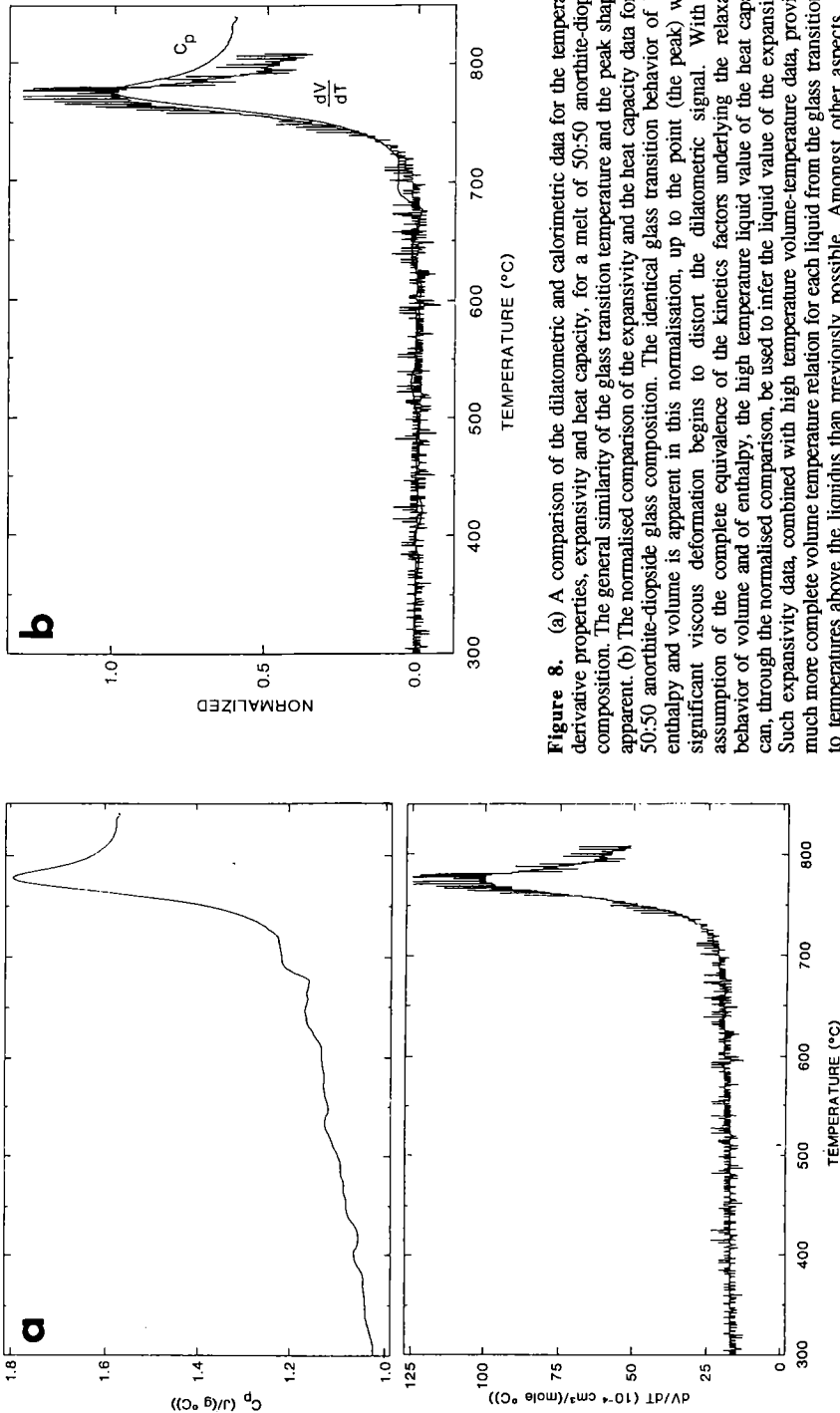


Figure 8. (a) A comparison of the dilatometric and calorimetric data for the temperature derivative properties, expansivity and heat capacity, for a melt of 50:50 anorthite-diopside composition. The general similarity of the glass transition temperature and the peak shape is apparent. (b) The normalised comparison of the expansivity and the heat capacity data for the 50:50 anorthite-diopside glass composition. The identical glass transition behavior of both enthalpy and volume is apparent in this normalisation, up to the point (the peak) where significant viscous deformation begins to distort the dilatometric signal. With the assumption of the complete equivalence of the kinetics factors underlying the relaxation behavior of volume and of enthalpy, the high temperature liquid value of the heat capacity can, through the normalised comparison, be used to infer the liquid value of the expansivity. Such expansivity data, combined with high temperature volume-temperature data, provide a much more complete volume temperature relation for each liquid from the glass transition up to temperatures above the liquidus than previously possible. Amongst other aspects, such determinations of the low temperature liquid expansivity have demonstrated for the first time the significant temperature dependence of the expansivity of some silicate melts. Reproduced with permission from Knoche et al. (1992a).

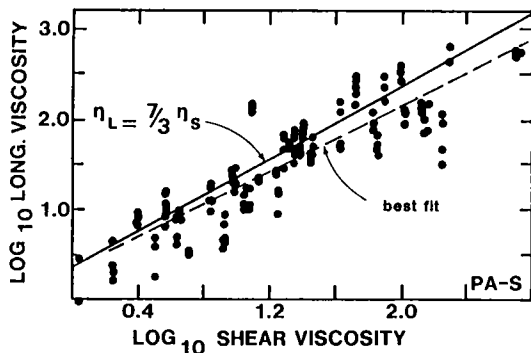


Figure 9. Longitudinal viscosity data derived from ultrasonic wave attenuation studies compared with shear viscosity data from concentric cylinder determinations. The agreement between the best fit to the data and the curve labelled $\eta_L = 7/3\eta_s$ indicates the equivalence of the volume and the shear viscosities for silicate melts. Reproduced from Dingwell and Webb (1989).

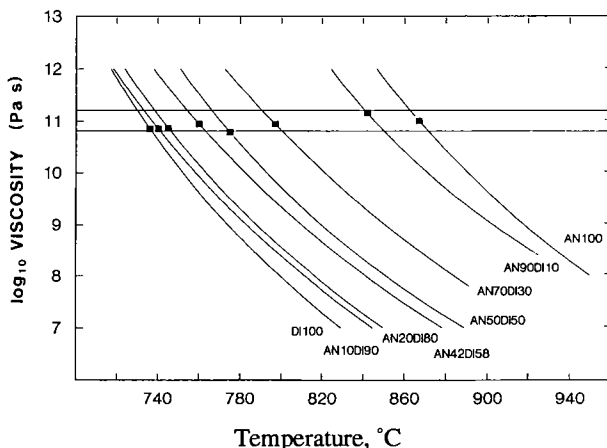


Figure 10. A comparison of calorimetrically determined glass transition temperatures and viscosity-temperature relationships for the system anorthite-diopside. The calorimetrically determined glass transition temperatures represent the peak temperatures from the transient values of heat capacity during heating in a scanning calorimeter. These T_g values correspond to viscosity values for each of the investigated melts that are equal within the uncertainties of the data sets. Thus the composition-dependence of the glass transition temperature can be described by an isokom or locus of points of equal viscosity for those compositions. Reproduced with permission from Knoche et al. (1992a).

If the volume and shear moduli and viscosities are similar or equal, then it seems inevitable that the relaxation times for shear and volume relaxation must be similar if not identical. Direct comparison of shear and volume relaxation times is not as simple as the comparison of volume and enthalpy discussed above. Nevertheless, the wealth of high quality shear viscosity data, together with our approximations regarding the shear modulus presented above, and the observations of the enthalpy-volume equivalence, allow a "short-cut" to the comparison of shear and volume relaxation times by comparison of the shear viscosity of various melts at a consistently defined glass transition temperature from scanning calorimetry. In short, if the shear relaxation time is identical to the volume and enthalpy relaxation times then, under the approximation of invariant shear modulus, the calorimetric glass transition temperature must represent an isokom or locus of constant viscosity for all melt compositions. This turns out to be a good approximation over wide ranges of melt composition. An example of this comparison is provided in Figure 10 for the system anorthite-diopside. The individual viscosity-temperature relations of the melts are each marked by a cross representing the calorimetric glass transition temperature. The crosses are distributed across Figure 10 at values of viscosity for the individual

compositions which do not vary outside the error of the determinations, describing instead an isokom of viscosity.

The demonstration of constant viscosity at a consistently defined calorimetric (or dilatometric) glass transition temperature implies that the shear relaxation time (which is proportional to viscosity through the Maxwell relation), is closely related to the enthalpy and volume relaxation times. A more exact comparison of the shear with the volume and enthalpy relaxation times is difficult because, as mentioned above, our choice of the definition of the glass transition as the peak temperature on the scanning traces is an arbitrary selection of a single feature which, although certainly a useful approximation to the glass transition temperature, does not exactly represent the fictive temperature of the melt as frozen in during cooling to form a glass. However, we have one more possibility to fix, for our purposes, the relation between the enthalpy and the shear stress relaxation times.

Studies of enthalpy relaxation in silicate glass melts have indicated that the activation energy of enthalpy relaxation is identical to that of viscous flow (e.g. Scherer, 1984). This leads to the following relationship between T_g and viscosity, which is independent of melt composition;

$$-\log_{10} |q| = A_{\text{DTA}} + \frac{E_{\text{DTA}}}{T_g} \quad (5)$$

$$\log_{10} \eta_s (\text{at } T_g) = A_\eta + \frac{E_\eta}{T_g} \quad (6)$$

(Moynihan et al., 1976) as the activation energies viscous flow E_η and enthalpy relaxation E_{DTA} are identical

$$\log_{10} \eta_s (\text{at } T_g) = \text{constant} - \log_{10} |q| = \log_{10} t (\text{at } T_g) + \log_{10} G \quad (7)$$

for shear relaxation time, t (s) and shear modulus G (Pa). Scherer (1984) found the constant to be 11.3 for η_s in $\log_{10}$ Pa s and quench rate $|q|$ in $^\circ\text{C s}^{-1}$. This relationship between viscosity and quench rate can be used to estimate melt viscosity at the glass transition. Stevenson et al. (1995) have performed rheological and calorimetric experiments to determine the value of the constant of Equation (7) for a number of rhyolitic obsidians. Their results are presented in Figure 11.

The viscosity-temperature and cooling rate-glass transition temperature relationships are Arrhenian for the obsidian compositions investigated by Stevenson et al. (1995). The activation energies obtained for viscous flow and enthalpy relaxation are identical for each sample. The value of the constant required in Equation (7) is 10.49 ± 0.13 ($1\sigma = 0.31$). Equation (7) can now be used to relate the cooling rate of volcanic melts to the viscosity at the glass transition.

As a first approximation, the shift factor K derived by Stevenson et al. (1995) (10.49 ± 0.13 ; $1\sigma = 0.31$) can be used for all silicic volcanic compositions. This shift factor is a revision of the zeroth order approximation of Dingwell and Webb (1990) based on an average shear modulus of 10 GPa. On closer inspection the data in Figure 11 raise the possibility that a slight compositional dependence of the shift factor may exist. Figure 12 displays the shift factor obtained by Stevenson et al. (1995) versus the agpaic index of those melts. The shift factor appears to increase with decreasing agpaic index. This minor variation in shift factor is within the 1σ estimate of fit quality. Nevertheless the variation

might reflect a melt structure influence on the relationship between the enthalpic relaxation time and the temperature of the peak in the C_p curve. Clearly a larger range of compositional variation needs to be investigated to address this possibility.

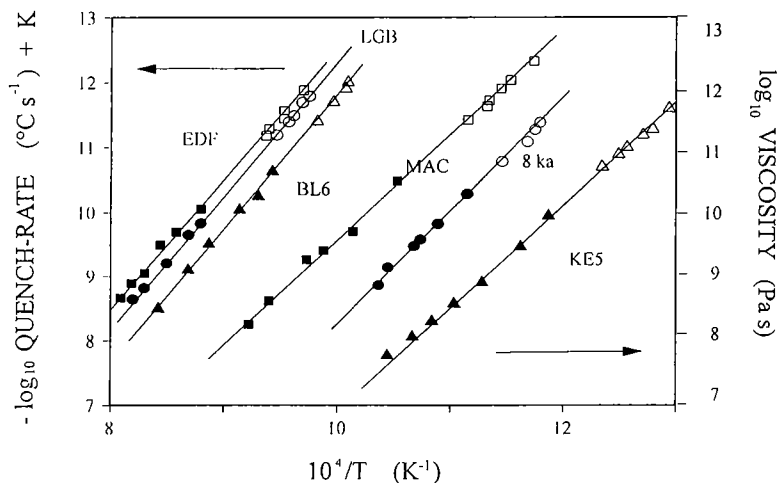


Figure 11. A comparison of the temperature-dependence of shear viscosity and the quench rate-dependence of the calorimetric (peak) glass transition temperature for six silicic volcanic obsidians. The identical activation energies exhibited by enthalpy relaxation (open symbols) and shear stress relaxation (solid symbols) together with several other lines of evidence lead to the inference that the same thermally activated process lies behind both phenomena. The two curves can be related through a logarithmic "shift factor" which then together with the Maxwell relation, explicitly relates cooling rate to relaxation time. Reproduced with permission from Stevenson et al. (1995). See that paper for identification of samples.

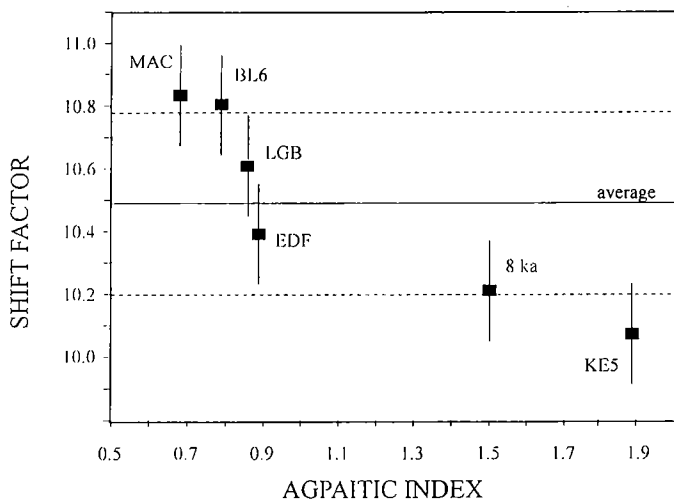


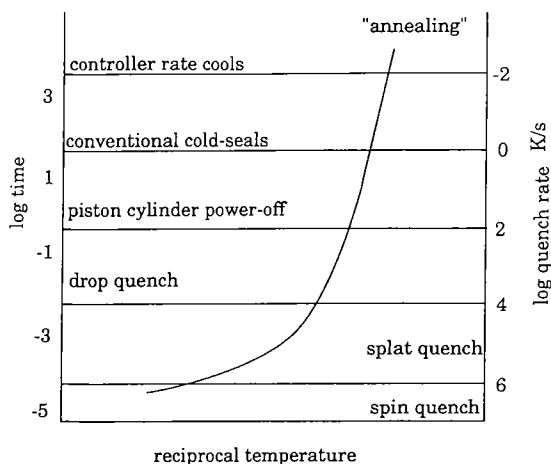
Figure 12. The shift factor derived in Figure 11 plotted versus the apaitic index of the investigated obsidians. The shift factor very slightly to lower values with increasing peralkalinity. The slight variation may indicate a subtle variation with composition of the relation between viscosity and calorimetric glass transition temperature. It is however very small in comparison to the uncertainties in the other parameters which must be combined with the shift factor to apply it to the estimation of the location of the glass transition during volcanic cooling. See the text for further discussion. Reproduced with permission from Stevenson et al. (1995).

Also worth noting in Figure 11 is the activation energy range obtained for these volcanic obsidians. The values of the slope of viscosity versus reciprocal temperature are relatively low. The activation energies exhibited by the compositions in Figure 11 yield a decadic variation in the viscosity over a temperature range of some 30°C. We will see later that this leads to a large variation in the glass transition temperature experienced by these samples in nature. The relatively low activation energy of relaxation for these melts is typical of relatively "strong" melts (melts for which the viscosity-temperature relationship is not very non-Arrhenian) in the high viscosity region (Angell, 1984). One of the greatest limitations of the concept of a glass transition temperature applied to geological melts is that, in comparison to most other classes of liquids, they are quite strong. For very fragile liquids, the non-Arrhenian viscosity-temperature relationship leads to such a large activation energy at glass transition timescales corresponding to moderate cooling rates that the glass transition approximates a single temperature value over a range of timescales. That this is clearly not the case for silicate melts is demonstrated in Figure 11. We are faced with the prospect that the glass transition temperature in volcanological processes must be specified for each cooling rate with all the implications that will have for volcanic facies-specific cooling rate variations.

An important distinction regarding the comparison between calorimetric and shear stress relaxation times presented above is that calorimetric and viscometric data (peak temperature and viscosity, respectively) are not necessarily monotonically proportional to the calorimetric and shear stress relaxation times, respectively. Why not? Firstly, the viscosity is related to the shear relaxation time (τ) through the Maxwell relation $\tau = \eta/G$, where G is the shear modulus. Tabulated data for the (low temperature) shear moduli of silicate glasses (Bansal and Doremus, 1986) indicate that significant differences in the shear modulus do exist but that such differences are unlikely to give rise to a total variation in shift factor of more than 0.1. Secondly, the "peak" temperature in a DTA trace is a complex function of the melt structure and the enthalpic relaxation time distribution (see below). It is thus possible that minor shifts in the calorimetric peak temperature are due to differences in the relaxation time distribution and the melt structure between different melt compositions such that the 1:1 relationship between the peak temperature and calorimetric relaxation time is lost as a function of melt structure. The result is a variable shift factor. This is not the equivalent of saying that the viscous relaxation time (or a single relaxation time approximation to the relaxation behavior yields a value that) is varying independently of the calorimetric relaxation time. As shown by the present agreement between the activation energies of viscous relaxation and enthalpic relaxation, the use of a fixed point on the calorimetric curve to define T_g results in the calculation of a correct (consistent) value for the activation energy (i.e. identical with that of shear relaxation), but suggests that the relaxation time associated with this point on the curve might vary as a function of the composition and the resulting kinetic parameters of the melt.

The fact that the shift factor Equation (7) for the relationship between enthalpy and shear stress relaxation explicitly includes a cooling rate can be used to determine the temperature at which a silicate melt will intersect the glass transition for a given cooling rate and to determine, from the activation energy of the viscosity, the sensitivity of the glass transition temperature experienced by the cooling sample to the rate at which it is cooled. The former calculation gives us the effective relaxation time corresponding to a given cooling rate and the latter allows us to evaluate the range of glass transition temperature likely to be experienced by a given volcanic melt during cooling in nature at differing rates in differing volcanic facies. The relationship between cooling technique for a variety of experimental methods and the log of the relaxation time for each case is illustrated in Figure 13.

Figure 13. A schematic description of the "hierarchy" of cooling rates normally obtained using a variety of techniques for the cooling or quenching of melts in research and industry. The slowest effective cooling rates achievable are obtained by programmed rate cools with electronic controllers. The fastest rates are achieved with so-called spin quench methods. The entire range of quench rate available to experimental labs is some eight orders of magnitude. The lower cooling rate end can be extended by simulating slower cooling rates using annealing experiments. The higher cooling rate end can be simulated in the quench of molecular dynamic simulations of melts.



The equivalence of enthalpic and volume relaxation times also lies behind several applications of relaxation to the study of silicate melts. Extensive data for the calorimetric and for the dilatometric relaxation of silicate melts now points clearly to identical peak temperatures during scanning measurements (calorimetric and dilatometric) on a wide range of melt compositions, an example of which has been provided in Figure 8. The equality of these peak temperatures indicates that the kinetic parameters controlling the relaxation time for the two investigated properties, enthalpy and volume, are indistinguishable from each other. This equivalence of relaxation time, combined with the observation presented above for the equivalence of shear stress and enthalpic relaxation times, appears to yield a relatively robust simplification of the estimation of the glass transition for the three important physical properties of igneous melts, viscosity, enthalpy and volume. Prediction of the glass transition for a given experiment or process in nature is then fully transferable between calorimetric, volumetric and rheological studies of silicate melts. This is a very powerful simplification and one which apparently does not hold for glassforming liquids in general (Angell, 1991). Nevertheless the tests provided above and the examples of applications provided below, illustrate that in addition to greatly simplifying the evaluation of the role of the glass transition in petrology and volcanology, it opens up new paths in the experimental investigation of silicate melt properties under difficult conditions.

Secondary relaxations

It has long been known that certain aspects of the structure of silicate melts induce relaxations at conditions well away from the glass transition in temperature-time space. These relaxations have been variably described as beta, secondary, detached, or decoupled relaxations. For silicate melts there is no evidence of such relaxations occurring in the liquid field above the glass transition at longer times and higher temperatures. Instead such relaxations occur invariably at lower temperatures for a given timescale or at shorter timescales for a given temperature, than the glass transition and are thus in the glass field defined in Figure 14. Such relaxations have lower activation energies than the glass transition. They are Arrhenian at temperatures lower than the glass transition for the timescale of the investigations. Under temperature-time conditions, however, where the melt structure experiences sufficient time to relax to the selected temperature on the timescale of the investigation of the secondary relaxation, the temperature dependence is non-Arrhenian. This is because it is influenced as it is by the temperature dependence of the melt structure. One of the best investigated examples of such a relaxation is the case of

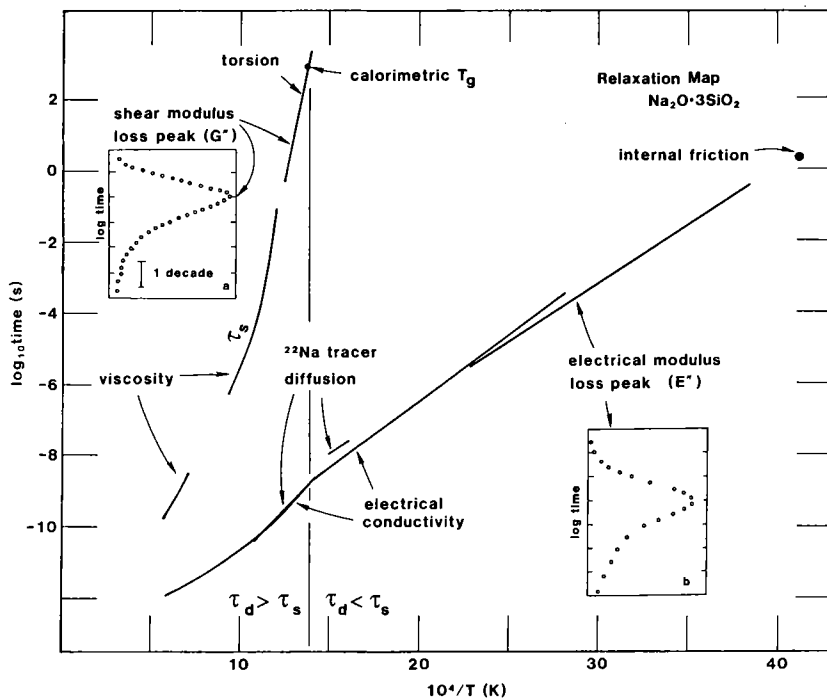


Figure 14. An example of a "relaxation map" for a silicate liquid. The diagram summarizes in an Arrhenian plot the location in time and in temperature of various relaxation modes in the silicate melt structure. Data on the temperature-timescale relationship for these relaxations come from calorimetric, dilatometric, viscometric, and electric property determinations. A detailed discussion of the data contributing to this diagram can be found in Dingwell (1990) from which this figure is reproduced.

alkali mobility in alkali silicate melts. Figure 14 illustrates a summary of data available for two relaxation modes in an alkali trisilicate melt. The secondary relaxation has a measurable expression in conduction of electricity as well as internal friction studies (see references in Dingwell, 1990). The electrical effect of alkali mobility is quite large as in other alkali-bearing melts whereas the internal friction effect is very small compared to the internal friction at the glass transition. Below, this presentation of relaxation modes as a relaxation "map" is used in the discussion of hydrous melts.

APPLICATIONS

Relaxation geospeedometry

Above it has been emphasized that great care must be taken to obtain identical thermal histories of melts before sensible comparisons of enthalpic, volume and shear stress relaxation are permitted. This sensitivity of the hysteresis in the glass transition interval to thermal history should be a potential source of information on the thermal history of glasses where it is not known. This hysteresis of melt properties in the glass transition interval stems from the path-dependence of the properties of the melt in passing from the glass to the liquid. Models for the empirical description of the transient variation or hysteresis of enthalpy in the glass transition interval have been proposed in order to quantify the relationship between hysteresis, material properties, thermal history and heating rate of measurement. These models form the basis of the application of scanning calorimetric

data to the determination of the cooling history of the volcanic glass, i.e. relaxation geospeedometry.

As noted above, if the cooling or heating rate, $|q|$, is viewed as a series of jumps of temperature ΔT which are followed by isothermal holds of duration Δt (i.e. $|q| = |\Delta T/\Delta t|$), it follows that a certain cooling rate corresponds to a certain time available for relaxation of the system. If the duration of Δt is relatively short (i.e. if the value of Δt approaches that of τ) then the time available for equilibration (relaxation) is no longer sufficient for relaxation (in this case backreaction of the structure with falling temperature) to permit further changes during cooling. Thus, when a glass is cooled below the glass transition a configuration (structure) is frozen into the glass, which can be correlated with a temperature at which the frozen structure corresponds to the equilibrium state. This is termed the fictive temperature, T_f , of the glass (Tool, 1946). The fictive temperature can be considered an order parameter for the description of the state of the system. Although subsequent experiments (e.g. Ritland, 1954) have demonstrated that complex thermal histories require more than a single order parameter to completely describe the relaxation behavior of glasses, the fictive temperature approximation yields remarkably good predictions of the bulk properties of quenched glasses. Therefore, this frozen structure, defining the fictive temperature, can be indirectly monitored by the study of its expression in any structurally-dependent property such as volume or (in the present case) enthalpy.

The onset of the glass transition upon cooling involves a change from a metastable equilibrium state ($T_f = T$) to a disequilibrium state ($T_f > T$) in a way which is illustrated with Figure 15. In Figure 15 the variation of the structural state of the liquid (indicated by variation in T_f) is illustrated for cooling and heating paths. At high temperature the melt is in equilibrium, described by $T_f = T$, whereas at low temperature the melt is not in equilibrium. During cooling, the path of T_f across the glass transition interval is marked by a departure from the equilibrium $T_f = T$ to a point where T_f becomes unaffected by temperature and the structure becomes frozen. When melts are rapidly quenched this departure from equilibrium occurs at a higher temperature and consequently a higher fictive temperature is frozen into the glass structure. For more slowly cooled glasses the melt remains in equilibrium to lower temperatures and thus lower values of fictive temperature are achieved. The glass structure (as represented by the fictive temperature, T_f) is therefore quench-rate-dependent with more rapid quench rates yielding higher values of T_f .

A hysteresis is observed between heating and cooling curves (Fig. 15). Cooling results in a gradual deviation from the equilibrium condition ($T_f = T$) until a constant value of fictive temperature ($T_f = \text{constant}$) below the transition, is reached. Reheating results in a

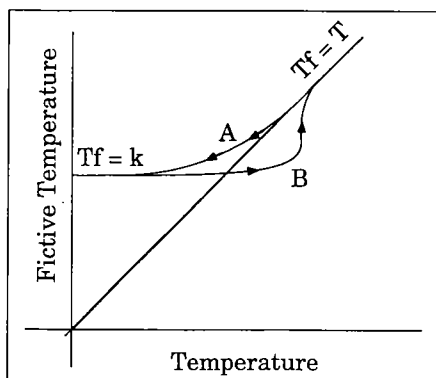


Figure 15. The variation of fictive temperature (T_f) with temperature (T) during the cooling and reheating of a melt. The derivative of the fictive temperature with respect to temperature goes from a value of 0 (T_f is constant) in the glassy state to a value of 1 ($T_f = T$) in the liquid state. This derivative is the normalisation basis for the comparison of the dilatometric and calorimetric data for the determination of liquid expansivity. Redrawn from Narayanaswamy (1971).

return to equilibrium via a path that is dependent on the heating rate, the previous cooling rate, the temperature dependence of structure and the temperature dependence of the relaxation time in the liquid. The detailed behavior of properties within the glass transition is a function of these parameters (Narayanaswamy, 1971; Moynihan et al., 1976a; Angell, 1988; Scherer, 1990; Angell, 1991).

If the value of some property, p (in our case enthalpy), is used to determine T_f , the value of T_f at temperature T is defined as;

$$\frac{\Delta T_f}{\Delta T} = \frac{\left[\left(\frac{dp}{dT} \right) - \left(\frac{dp}{dT} \right)_g \right]_{T_f}}{\left[\left(\frac{dp}{dT} \right)_e - \left(\frac{dp}{dT} \right)_g \right]_{T_f}} \quad (6)$$

where the subscripts "e" and "g" refer to the equilibrium liquid and the glass respectively (Scherer, 1984). T_f can be used to describe the property during changes in temperature (T) and time (t). In order to calculate T_f as a function of increasing temperature it is necessary to define the form of the relaxation equation and the form of the relaxation time as a function of temperature. An empirical expression for the relaxation process in silicate melts is the Kohlrausch-William-Watts "stretched exponential" function (KWW, Scherer, 1984)

$$p = p_0 \exp[-(t/\tau_{ok})^\beta] \quad (7)$$

where τ_{ok} is the characteristic relaxation time and β is a constant ($0 < \beta \leq 1$). The KWW function has been found to give an excellent fit to a wide range of relaxation processes (DeBolt et al., 1976). Lower values of β indicate a broader spectrum of relaxation times. The evolution of the fictive temperature and the related property can be written as

$$T_m = T_0 + \sum_{j=1}^m \Delta T_j \left[1 - \exp \left(- \left(\sum_{k=j}^m \Delta T_k / |q_k| \tau_{ok} \right)^\beta \right) \right] \quad (8)$$

for temperature T_0 above the glass transition and temperature steps ΔT , heating (or cooling) rate $|q|$, and relaxation time τ_{ok} (DeBolt et al., 1976). This is the basic equation used in the present study to model the evolution of T_f and enthalpy across the glass transition interval.

Evidence has been reviewed above supporting the statement that the relaxation of enthalpy, volume, and shear stress all have the same timescales. This is supported by a number of investigations (DeBolt et al., 1976; Scherer 1984a,b, 1986, 1990; Stevenson et al., 1995; Hess et al., 1995). Following Narayanaswamy (1971, 1988) an Arrhenian form of the relaxation time equation with terms for the (temperature-dependent) structural contribution and the thermal contribution to the relaxation is used

$$\tau_p = \tau_0 \exp \left[\frac{xH}{RT} + \frac{(1-x)H}{RT_{fp}} \right] \quad (9)$$

where H is the activation enthalpy, R is the gas constant and x is a constant with $0 \leq x \leq 1$. H is equal to the activation energy for shear viscosity in the glass transition interval. When $x=1$ there is only a thermal contribution to the relaxation time. As x approaches zero there is an increasing contribution of the temperature dependence of the structure to the calculated relaxation time. This description of the temperature dependence of the relaxation time

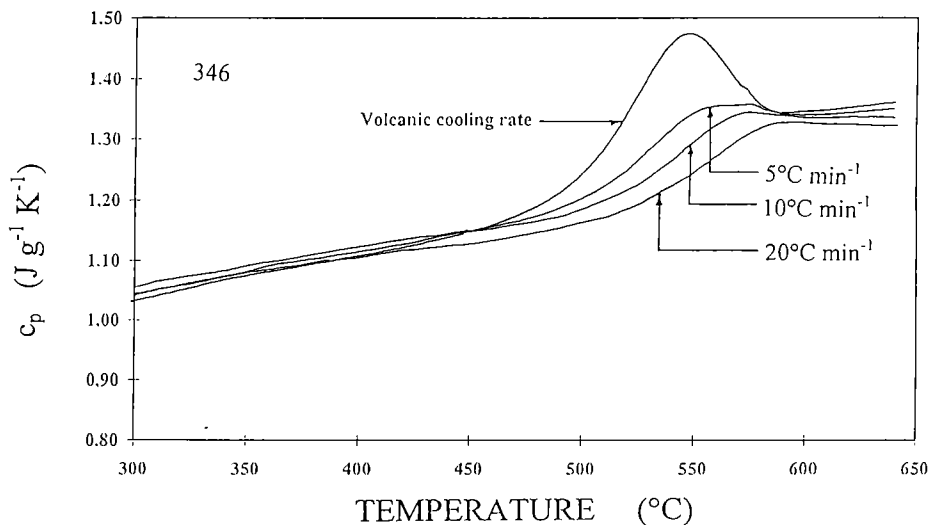


Figure 16. The heat capacity of a volcanic obsidian obtained with samples of differing thermal history. The known cooling rates of 20, 10 and 5°C/min were generated within the scanning calorimeter and the unknown cooling rate is continues the trend of the known cooling rates to a lower apparent cooling rate. The quantification of the hysteresis in the transient segment of the heat capacity at the glass transition is the method discussed in the text for the characterisation of the thermal history of the natural glass in terms of an apparent linear cooling rate across the glass transition using the concept of relaxation geospeedometry. Reproduced from Wilding et al. (1995).

results in a four parameter structural relaxation model; with x and β unknown, τ_0 estimated from Equation (1), and H the activation energy calculated from Equation (6).

Of the four natural compositions investigated by Wilding et al. (1995), one sample, a phonolite from Montaña Rajada, Tenerife, is a massive obsidian from one of the more recent flows. Two compositions from lava flows within the Greater Olkaria Volcanic Complex (GOVC), Kenya, are peralkaline rhyolites with agpaaitic indices (A.I.) of 1.0 and 1.3 and the fourth composition is a pantellerite from the Eburru Complex, adjacent to the GOVC. The pantellerite occurs as a thin band of glass 0.5 m thick and 10 m in lateral extent within a poorly structured, proximal air fall deposit.

The experimental details of the present application of the experimental determination of cooling rate by scanning calorimetry have been presented in full by Wilding et al. (1995). They are summarized briefly here. The heat capacity of each raw sample was determined to $\sim 50^\circ\text{C}$ above the glass transition temperature at a heating rate of 5°C min^{-1} . The heat capacity for a natural glass is shown in Figure 16. This heat capacity data was subsequently used to determine the cooling rate of the natural glass. Central to the successful application of this method to volcanic glasses is a reliable estimate of their material specific parameters. These are obtained to be input into the fitting of calorimetric data for the determination of cooling rate by the adoption of an internal calibration procedure. Such an internal calibration is performed by recording the heat capacity curves of the sample with matched, known cooling and heating rates of 4, 5, 8, 10, 16, 20 and $32^\circ\text{C min}^{-1}$. Sample integrity during measurement was confirmed by bulk chemical analyses, ^{57}Fe Mössbauer spectroscopy (oxidation state), and infrared absorption spectroscopy (water content). Examples of the heat capacity data for the sample "346" obtained under such conditions are included in Figure 16. The temperature at which the peak in the heat capacity curve occurs increases by more than 40°C with this increase in

matched cooling and heating rates. The activation energy of enthalpy relaxation for each sample was then calculated from the known heating rate and measured peak temperature T_g ;

$$-\log_{10}|q| = -\log_{10}|q_0| + \frac{H}{RT_g}. \quad (10)$$

This treatment enables the derivation of the activation energy for enthalpic relaxation (H) through the relationship between quench rate, $|q|$, and reciprocal T_g .

The modeled c_p curves are expressed in terms of a normalized diagram (Fig. 17a,b,c) which makes reference to the fictive temperature in the glass and liquid fields. In this sample, "DP1", the modeled cooling rate of $0.8 \times 10^{-3} \text{ }^\circ\text{C s}^{-1}$ is shown in comparison with the c_p trace for the raw glass on reheating (Fig. 17a). In addition modeled heat capacity curves which differ by 1 $\log_{10}$ unit are shown i.e. $0.8 \times 10^{-2} \text{ }^\circ\text{C s}^{-1}$ (Fig. 17b) and $0.8 \times 10^{-4} \text{ }^\circ\text{C s}^{-1}$ (Fig. 17c). The results of the modeled cooling rates are demonstrated in Figure 18. Each modeled cooling rate is shown with the calibration range, that is the range of quench rates in the subsequent calorimetry measurements. The slope of each line is related to the activation energy of enthalpic relaxation..

Four very different cooling rates have been obtained for the four different compositions. The most slowly cooled natural sample is the most rhyolitic and has the highest viscosity. The two samples of the more peralkaline rhyolite, "346", have different modeled cooling rates which we interpret as differences in the thermal geometry of the lava flow. The difference of a factor of 10 is greater than the reproducibility of the measurements and model (Fig. 18) and for this relatively viscous sample cooling may have varied over relatively small distances.

Both the samples of the phonolite, "DP1" have comparable cooling rates, as do the samples of the pantellerite, "KE5". The latter sample has a very slow modeled cooling rate of the order of $2 \times 10^{-5} \text{ }^\circ\text{C s}^{-1}$, equivalent to 2°C d^{-1} . The field occurrence of this sample suggests emplacement as a welded horizon within an air fall pumice, Wilding et al. (1995) have interpreted the relatively slow cooling rate as the result of slow dissipation of heat from a relatively thick volcanic pile possibly resulting from a reheating of the rapidly cooled sample due to its primary burial within hot pyroclastics. This last aspect raises the important point that should volcanic samples be reheated at conditions sufficiently above the glass transition that total relaxation occurs, then all evidence of the primary cooling rate may be lost. The recorded state of the glass structure would in the case of such a double cooling cycle (or a multiple cooling cycle) which involves excursions above the glass transition, only record information on the last cooling cycle. If the annealing of a volcanic sample involves partial relaxation near the glass transition then the result may be a very complex signal from more than one cycle of the cooling history.

In further analysis of facies-specific samples of a very wide range of phonolite samples from Tenerife, Wilding et al. (in prep.) have identified a range in effective cooling rate of over four orders of magnitude from less than a degree per day to ten degrees per second, or 0.0001°C/s to 10°C/s . A very similar range (0.0003°C/s to 5.5°C/s) of effective cooling rates has been obtained by Zhang et al. (1995) for calcalkaline rhyolites from California based on entirely different data. This equivalence of cooling rates estimated from property relaxation (Wilding et al., 1995) and from hydrous species relaxation (Zhang et al., 1995) serves to underline the point (see also below) that the relaxation of properties and structures in silicate melts are intimately linked.

Equation of state: liquid expansivity and volume

The next application of melt relaxation involves the premise that not only the relaxation times of various properties are equivalent but also the details of the relaxation

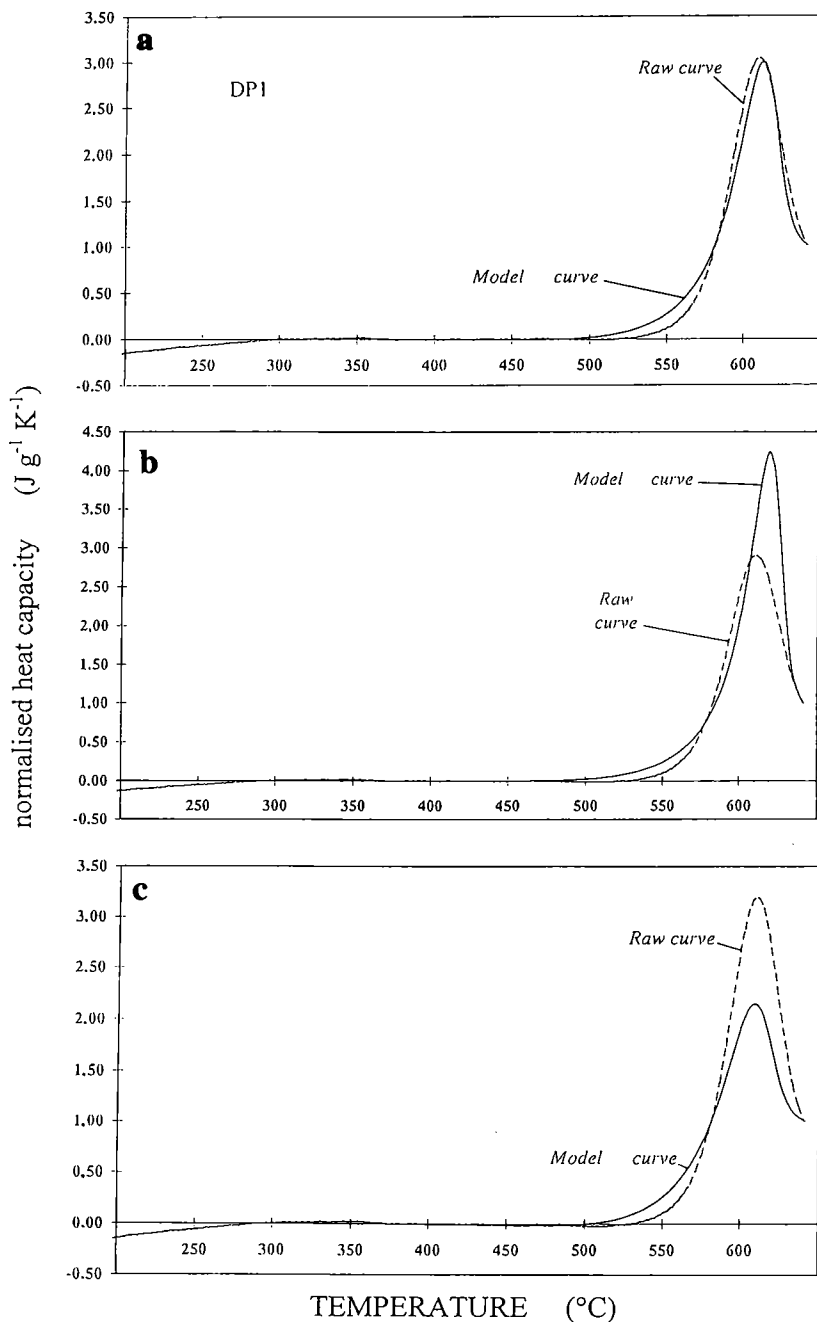


Figure 17. The results of modeling the transient values of the heat capacity in the glass transition range using the algorithm and parameters described in the text. An adjustment of the cooling rate value (representing predicted thermal history) by 1 order of magnitude lower (b) or higher (c) produces a serious mismatch, the severity of which is an indication of the sensitivity of the calorimetric hysteresis to the cooling rates obtained. Reproduced with permission from Wilding et al. (1995).

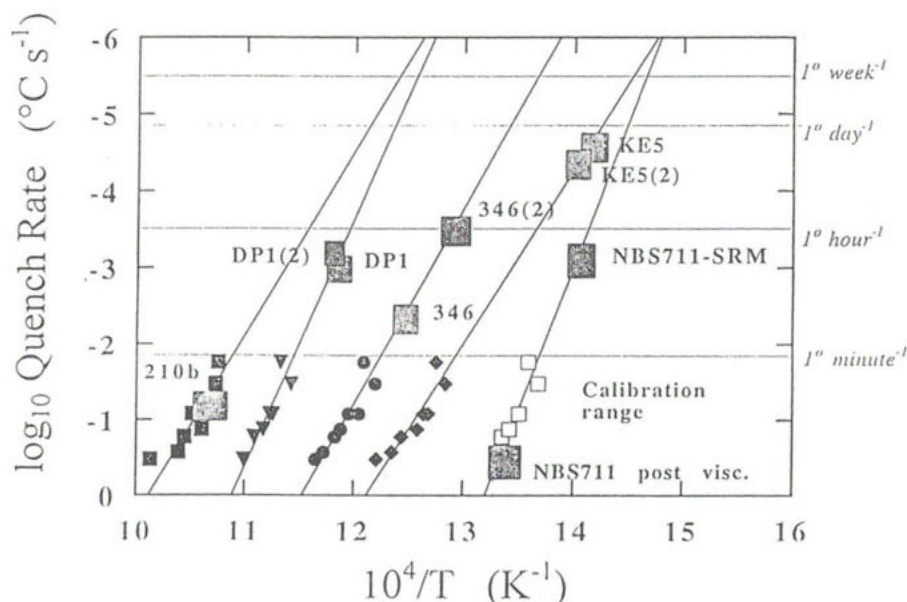


Figure 18. The logarithm of the quench rate versus the reciprocal of the absolute temperature for five investigated volcanic obsidians. The calibration range of the range of heating/cooling rates accessed by the scanning calorimeter is indicated in the small symbols for each composition. From the variation of the calorimetric glass transition temperature with heating/cooling rate, the enthalpy of the relaxation process can be estimated. This estimation provides the preexponential and activation energy parameters for the temperature dependence of the relaxation time. The modelled cooling rates for the naturally cooled glasses are the vertical positions of the large boxes. The temperatures which correspond to the intersections of these cooling rates and the slopes of each composition represent the glass transition temperature that each melt experienced during cooling in nature. The range of cooling rates estimated from these compositions originating from differing volcanic facies is four logarithmic units (from faster than 1 K/min to approximately 1 K/day). Reproduced with permission from Wilding et al. (1995).

process in the glass transition interval. The theory of obtaining relaxed-liquid molar expansivity data from a combination of scanning calorimetry and dilatometry, the application presented here, has its origins in that premise. It was introduced by Webb et al. (1992) and is described in full in that study. Here we review the method and its results to date.

The comparison of dilatometric and calorimetric measurements is based on the principle that the relaxation of melt properties in the glass transition region can be described by a universal set of parameters. These universal parameters can be derived from the relaxation of one property (in this case enthalpy) and then applied to predict the behavior of a second property, such as volume. Heat capacity is measured through the glass transition and molar expansivity up to the glass transition using differential scanning calorimetry and dilatometry, respectively. The normalized calorimeter trace is then applied to the molar expansivity curve to extend it into the liquid region.

It has been emphasized above that silicate glasses quenched from liquids preserve a configuration that can be approximated to the equilibrium structure of the liquid at some fictive temperature, T_f (Tool and Eichlin, 1931). To describe in general, the relaxed (liquid) or unrelaxed (glassy) properties of a silicate melt it is necessary to specify the temperature and the fictive temperature of the melt. The temperature derivative of the physical properties of a glass and a liquid (e.g. molar heat capacity (dH/dT) and molar thermal expansivity

(dV/dT) can be used to describe the temperature-derivative of the fictive temperature. To do this, the temperature-derivative of any property in the glass transition interval (e.g. enthalpy, volume) is normalized with respect to the temperature-derivative of the liquid and glassy properties. Assuming the equivalence in relaxation time and activation energy for volume and enthalpy relaxation for melts with identical thermal histories, the temperature derivatives of the fictive temperature T_f , the enthalpy (H) and volume (V) can be related by:

$$\frac{c_p(T_f) - c_{pg}(T_f)}{c_{pe}(T_f) - c_{pg}(T_f)} = \frac{dT_f}{dT} \bigg|_{T_f} = \frac{\left(\frac{dV(T)}{dT} - \frac{dV_g(T)}{dT} \right) \bigg|_{T_f}}{\left(\frac{dV_e(T)}{dT} - \frac{dV_g(T)}{dT} \right) \bigg|_{T_f}} \quad (11)$$

Thus, in the glass transition region, the behavior of any temperature-dependent property of a melt can be predicted from the known behavior of another temperature-dependent property if the relaxation of the two properties is equivalent. In the above equation, which relates c_p and thermal expansivity dV/dT , the only unknown parameter is the thermal expansivity of the relaxed liquid at temperature T in the glass transition interval.

Due to the lack of relaxed thermal expansivity data (viscous flow of the melt above T_g results in the inability to determine volume as a function of temperature), the liquid molar thermal expansivity must be calculated from the dilatometric trace by normalizing both the scanning calorimetric and dilatometric data:

$$P'(T) = \frac{P(T) - P_g(T)}{P_p - P_g(T)} \quad (12)$$

where the subscripts "p" and "g" refer to peak and unrelaxed, glassy values. The relaxed value of thermal expansivity can now be generated from the peak and extrapolated glassy values of thermal expansivity; the volume and coefficient of volume thermal expansion α_v [$1/V(dV/dT)$] of the melt can be calculated.

Small changes in composition or fictive temperature of a silicate melt can strongly influence relaxation behavior. Thus the above method only can be applied to calorimetric and dilatometric data obtained on the same sample using identical experimental conditions and thermal histories. It is only this internal consistency that permits the use of the assumption of the equivalence of the enthalpy and volume relaxation behavior.

The investigation of a variety of synthetic melt compositions using the methods of determination of the expansivity and volume of the melt just above the glass transition have yielded results which may be generalized to the following conclusions. The volume and expansivity data obtained near the glass transition are consistent with the volume and expansivity data obtained with immersion methods at higher temperatures. This is not to say however that the volume and expansivity data are similar in magnitude. Figure 19 illustrates the point well for the example of GeO_2 . The curve is a combined fit to the volume and expansivity data of Dingwell et al. (1993c) and those of Sekiya et al. (1980). Clearly the low and high temperature data are reconcilable with a smooth nonlinear volume-temperature relationship. Note that the segment superimposed on the curve near the glass transition is the expansivity value determined from the low temperature technique described above. The agreement between that expansivity value and the fitted curve is evident.

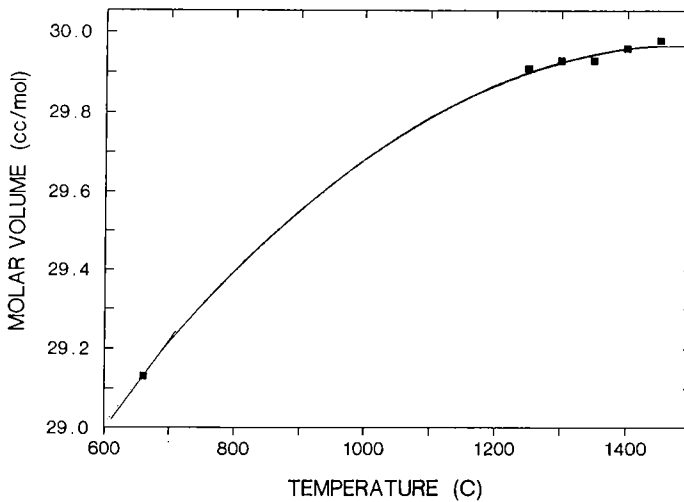


Figure 19. Temperature dependence of volume of GeO_2 liquid determined by the dilatometric/calorimetric method described in the text as well as the double-bob buoyancy method. The nonlinearity of the curve fitted to both expansivity data sets is corroborated by the expansivity segment near the glass transition illustrating the value derived for the liquid just above the glass transition. The agreement between the dilatometric/calorimetric estimate of the expansivity, the buoyancy-derived value, and the values derived from the volume-temperature fit to both data sets, is excellent. Reproduced from Dingwell et al. (1993c).

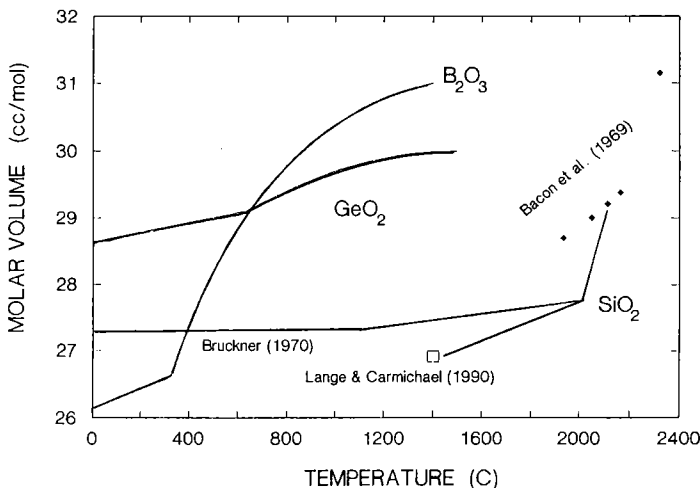


Figure 20. A summary of the estimates of volume-temperature relationships available for a number of simple oxide liquids stable at high temperatures. B_2O_3 and GeO_2 exhibit strongly decreasing expansivities with increasing temperature such that the high temperature liquid expansivities of the liquids are comparable to the glassy expansivities. SiO_2 is poorly constrained. The glassy expansivity and indirect estimates of the liquid expansivity at low temperature (Knoche et al., 1994, see text) indicate very low values. The high temperature single bob buoyancy data of Bacon et al. (1960) point to a higher expansivity for SiO_2 which would generate a volume temperature relation intersecting the low temperature glassy expansivity curve at reasonable estimates of the glass transition temperature (see text for discussion). Reproduced from Dingwell et al. (1993c).

The temperature dependence of the expansivity of melts is, in general, nonzero. Figure 20 illustrates the temperature dependence of the volume for B_2O_3 , GeO_2 and SiO_2 . The data for B_2O_3 are all obtained in the stable liquid state and indicate a strong decrease in the expansivity with temperature, the GeO_2 data behave similarly. The available data for the temperature dependence of the volume of SiO_2 are of extreme theoretical and practical importance to geochemistry but very poorly constrained. The glassy expansivity is very low (Brückner, 1970), whereas the only liquid data available indicate a significantly strong expansivity at higher temperatures. One might argue that an extraordinary effect at the glass transition temperature could yield high liquid expansivity data of SiO_2 even at temperatures just above the glass transition, but at least one strong argument exists against it. Knoche et al.'s (1994) study of melts in the system Na_2O-SiO_2 , ranging in composition up to 98% SiO_2 indicate, by partial molar arguments, that the liquid expansivity of SiO_2 is indeed very low at low and at high temperatures (Fig. 21). Whether the expansivity of SiO_2 liquid increases with temperature remains an important question for future investigation.

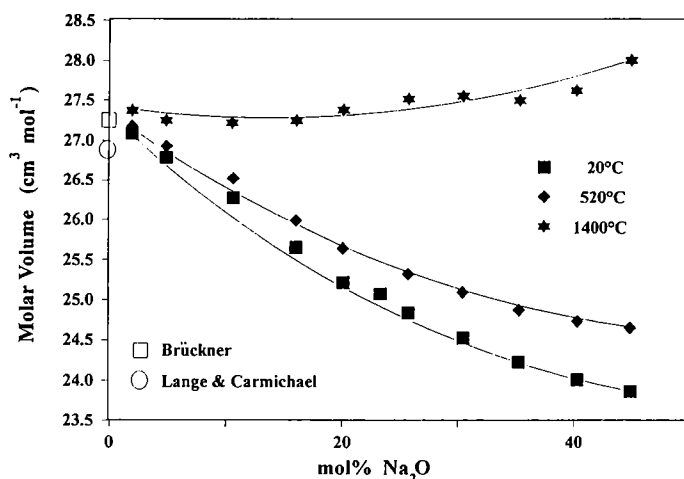


Figure 21. Melt volumes in the Na_2O-SiO_2 system at temperatures of 20°C (glass) as well as 520° and 1400°C (liquid). The data range from 45 to 2 wt % Na_2O and clearly indicate the very low expansivity of SiO_2 liquid in the temperature range from 520° to 1400°C but the expansivity of these liquids does not go to zero at a finite SiO_2 concentration as suggested by the work of Bockris et al. (1955). Such derivations of the relaxed partial molar volumes of inaccessible liquids (e.g. SiO_2 at 520°C) are a result of the dilatometric/calorimetric determination of melt volume and expansivity. Reproduced with permission from Knoche et al. (1994).

As can be seen from Figure 20, the expansivity of the liquid phase can be comparable to that of the glass phase. Data for the albite-anorthite-diopside system (Fig. 22) illustrate this well. The glassy and the high temperature liquid expansivity data are similar whereas the liquid expansivity data just above the glass transition temperature are significantly higher than either. This increasing contraction of the melt volume with falling temperature approaching the glass transition appears, where it is strong, almost as if it were recording an impending structural catastrophe for the liquid which is warded off by the intervention of the glass transition temperature - a volume equivalent of a Kauzmann catastrophe?

The example of the Na_2O-SiO_2 system above brings us to the next application of the determination of melt expansivity using the dilatometric/calorimetric method. High precision, high temperature determinations of the densities of silicate liquids have thus been the subject of several experimental studies in the geosciences (Lange and Carmichael, 1987; Dingwell et al., 1988; Dingwell and Brearley, 1988; Dingwell, 1992) and empirical predictive schemes have been proposed (Lange and Carmichael, 1987; 1990; Kress and

Carmichael, 1991). Up to the present, such experimental studies have been focused on the determination of melt density at 1 atm pressure and superliquidus temperatures using double bob Archimedean methods (e.g. Dingwell et al., 1988) as well as high pressure studies using Stokesian falling sphere or sink-float densitometry (Kushiro, 1978a,b; Scarfe et al., 1987). Notable exceptions are the shock-wave Hugoniot density studies (Rigden et al., 1984; 1988; 1989), ultrasonic compressibility studies (Rivers and Carmichael, 1987; Kress et al., 1988; Webb and Dingwell, 1994) and inferences from the slopes of melting curves (e.g. see Lange, 1994), although in some of these studies the question of melt relaxation is not adequately addressed (see discussion by Dingwell and Webb, 1989).

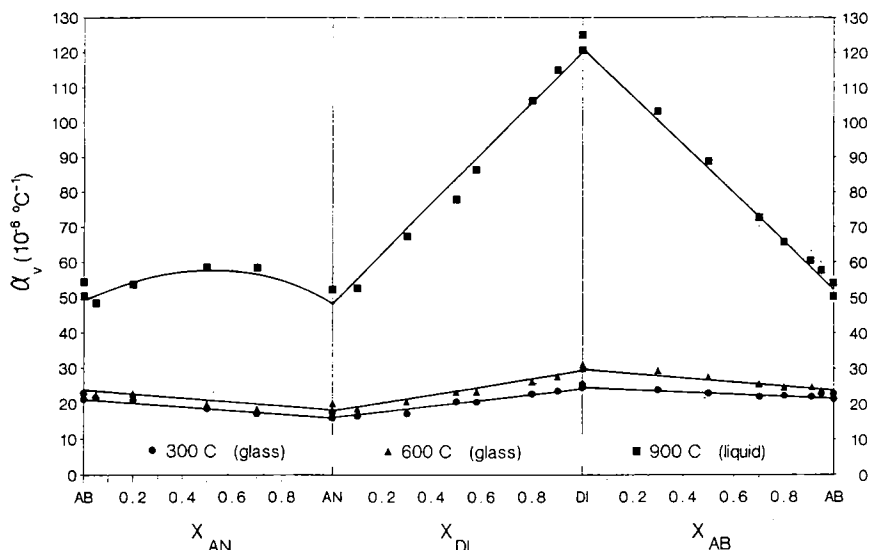


Figure 22. The expansivities of melts in the system albite-anorthite diopside derived by the methods outlined in Figure 16 as well as buoyancy methods at higher temperatures. The composition-dependence of the expansivity is largest at 900°C, just above the glass transition of melts in this system. The high temperature expansivities of the liquid match are similar to the glassy values of expansivity in this system. The "anomalous" high expansivities just above the glass transition may in fact be a reflection of structural constraints leading to the onset of the glass transition. Reproduced with permission from Knoche et al. (1992c).

The vast majority of the above work has concentrated on basic to intermediate melt compositions at the temperatures and pressures relative to the petrogenesis of basalts, andesites and derivative composition. Another branch of igneous petrogenesis, giving rise to intrusive granitic complexes and to more evolved pegmatitic is relatively under-investigated (cf. Knoche et al., 1992b; Dingwell et al., 1993b).

Knoche et al. (1995) have generated a low temperature multicomponent model for the densities of leucogranitic and pegmatitic melts. The densities and thermal expansivities of 39 haplogranitic silicate melts have been experimentally determined. The compositions represent the additions of selected oxide components Al_2O_3 , Cs_2O , Rb_2O , K_2O , Na_2O , Li_2O , BaO , SrO , CaO , MgO , TiO_2 , Ta_2O_5 , Nb_2O_5 , F_2O_{-1} , P_2O_5 , B_2O_3 and WO_3 to a base composition of haplogranitic (HPG8) composition. The example of the effects of the addition of alkalis and alkaline earths to the volume of leucogranitic melt at 750°C are illustrated in Figure 23.

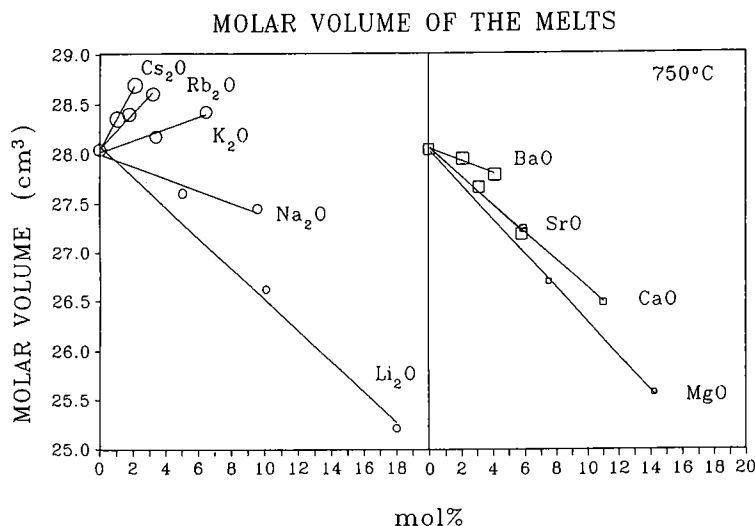


Figure 23. Plots illustrating the effects of the addition of alkalis and alkaline earths to the molar volume of a haplogranitic melt. The variation in molar volume has been derived for an isotherm of 750°C using a linear approximation to the melt expansivity in the temperature range from the glass transition to 750°C and employing the value of the expansivity obtained at the glass transition using the dilatometric/calorimetric method. Such volume data have been incorporated into the multilinear regression of oxide volumes for the determination of partial molar volumes of oxide components of leucogranitic and pegmatitic melt densities by Knoche et al. (1995).

The partial molar volumes were obtained by a least squares fits to a multicomponent linear dependence on the oxide concentrations. The results of the fit are the set of partial molar volumes for the oxide components at 750°C and expansivities of these partial molar volumes in Knoche et al. (1995). The residuals on the fit indicate that the root mean squared deviation is 0.24 cm³/mole or approximately 0.3% of the specific volumes of these melts. This quality of fit indicates that further terms involving nonlinear oxide contributions to the volume are not required. The partial molar volumes range from 10.53 ± 0.29 cm³/mole for MgO to 69.09 ± 1.82 cm³/mole for Ta₂O₅. Compared on the basis of one oxygen per mole they range from 10.53 ± 0.29 cm³/mole (MgO) to 55.38 ± 1.69 cm³/mole (Cs₂O).

The partial molar volumes provided by Lange and Carmichael (1990) from high temperature determinations have been compared at 750°C. Considering that this is a gross extrapolation of the Lange and Carmichael (1990) model, the agreement is not bad with one exception, TiO₂. The origin of the discrepancy for TiO₂ lies almost certainly in the composition dependence of the structural role of TiO₂ (Mysen, 1988; Dingwell et al., 1994). Several spectroscopic studies of Ti-rich silicate glasses indicate that the average coordination number of Ti decreases in the presence of Na and K. The consequences of the shift in coordination number include anomalous heat capacity (Richet and Bottinga, 1986; Lange and Navrotsky, 1993); anomalous compressibility-volume systematics (Webb and Dingwell, 1994) and a variable partial molar volume for TiO₂ in high temperature alkali and alkaline earth silicate melts (Dingwell, 1993). Thus granitic melt chemistry may stabilize an lower mean coordination number for Ti than is the case for alkali- and alkaline earth silicate melts (Dingwell et al., 1994; Paris et al., 1994a). In fact more recent X-ray absorption spectroscopic data on the effect of the addition of Al to alkali silicate melts indicates a growth in spectral features associated with a tetrahedral coordination of Ti, that is a lower

average coordination than that observed in the simple Al-free melt compositions observed to date (Paris et al., 1994b).

Negative expansivities are obtained for TiO_2 , Al_2O_3 , WO_3 , P_2O_5 and Nb_2O_5 . These are all high field strength elements. Melt compositional dependence of the structural roles of Al_2O_3 , TiO_2 and P_2O_5 have all been repeatedly proposed in the past based on spectroscopy, phase equilibria, thermochemistry or physical property behavior (see summary in Mysen, 1988). Recent high temperature density data for melts in a large compositional range of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system (Courtial and Dingwell, 1995) also indicate a negative expansivity of the Al_2O_3 component when treated without excess terms. The compositional variation of the volumetric behavior of TiO_2 is discussed above. Diffusivity and viscometry data (Chakraborty and Dingwell, 1993; Toplis and Dingwell, 1994) together with spectroscopic observations by Gan and Hess (1992) and solubility data for apatite and other phosphate minerals (Rapp and Watson, 1986; Montel, 1986; Pichavant et al., 1992) all indicate that the structural role of P_2O_5 is variable. High-field strength elements appear in general to be capable of adopting variable coordination based on the available complexing cations. Although little is known for WO_3 or Nb_2O_5 , recent X-ray spectroscopic data for Nb_2O_5 indicate a variable coordination of Nb as well in silicate glasses, but, interestingly, not for Ta_2O_5 (Paris, pers. comm.), which here exhibits a positive expansivity.

Relaxation and rheology

The observation of Newtonian viscosity implies that the thermodynamic state of the melt is independent of the applied stress. The simplest microscopic interpretation of this behavior is that the self diffusive motion of atoms due to random thermal fluctuations in the melt is greater than that imposed by the experimental strain rate. With decreasing temperature the self diffusivities of the melt components decrease and, if a sufficiently high strain rate can be maintained experimentally, the relative motion of atoms required by this experimental strain rate approaches that due to self diffusion. The immediate result is a decrease in the measured viscosity with increasing strain rate, i.e. non-Newtonian flow. Experimentally, non-Newtonian flow of silicate melts has been observed using frequency domain (e.g. ultrasonic) and time domain (e.g. dilatometry) methods. The frequency domain methods operate at very low strains and are capable of mapping the viscoelastic response of silicate melts up to fully elastic behavior. They are discussed in the chapter by Webb and Dingwell. Here we turn our attention to the latter dilatometric studies.

Several types of dilatometric experiments have been performed which record the onset of non-Newtonian viscosity in silicate melts. The first example is fiber elongation dilatometry. Li and Uhlmann (1970) suspended long silicate melt fibers through a tube furnace with a load hanging from the lower end. They determined the onset of non-Newtonian flow for a Rb-silicate melt. At certain stresses and temperatures, the strain rate of elongation increased as the fiber drove into non-Newtonian rheology. This effect was observed to be runaway. Webb and Dingwell (1990a,b) extended these observations using a slightly modified fiber elongation technique in which the entire fiber was contained in the hot zone of the dilatometer furnace. Webb and Dingwell (1990a,b) surveyed a range of natural and synthetic silicate melt compositions using this method. The viscosity results for synthetic and natural melts are presented in Figures 24 and 25. The strain-rate deviates from the linear dependence of slope 1 on stress at approx. 10^8 Pa (Fig. 24). The calculated viscosities are presented in Figure 25 as functions of the strain rate. The decrease in viscosity (non-Newtonian flow) begins at $\sim 10^{-4}$ s⁻¹. Webb and Dingwell (1990a) demonstrated that the onset of non-Newtonian flow for the entire range of silicate melt compositions investigated could be reduced to a single curve of viscosity versus "reduced" strain rate $\dot{\epsilon}'/\epsilon_T$ where ϵ_T is the inverse of the shear relaxation time

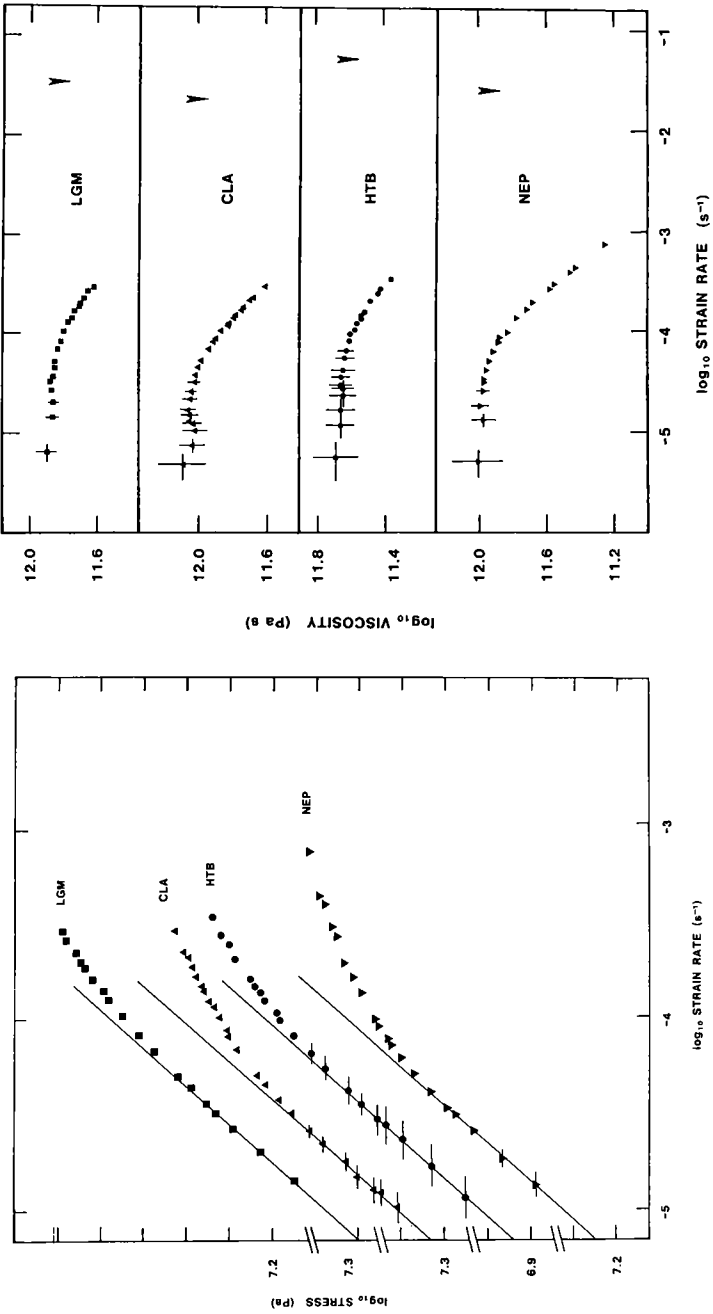


Figure 24 (left). The onset of non-Newtonian viscosity in four natural melt compositions, a rhyolite, andesite, basalt and nephelinite, as well as NBS 710 soda-lime glassmelt. The deviation of the stress strain rate relation from 1:1 heralds the onset of the nonNewtonian behavior. Reproduced from Webb and Dingwell (1990b).

Figure 25 (right). The deviation of the calculated viscosity of the same four natural melt compositions from a constant Newtonian value at low strain rates to yield a decreasing value through a process empirically described as "shear thinning". The decrease of viscosity calculated from these fiber elongation viscosity determinations reached a viscosity decrease of a half log unit before brittle failure or instrumental limits terminated the experiment. Reproduced from Webb and Dingwell (1990b).