

## LETTERS

### Thermal expansion of silicate liquids: Direct determination using container-based dilatometry

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#### ABSTRACT

The expansivity of a silicate melt in the relaxed liquid state was obtained by direct dilatometric measurement for the first time. During the measurement, the liquid sample resides within a metal container composed of a hollow cylinder and two solid cylindrical end pieces. The sample is loaded at room temperature as a precisely machined glass cylinder. Heating the assembly beyond the glass transition results in an intimate space-filling seal of the liquid to the container surfaces. At temperatures above the glass transition, the linear expansion of the combined assembly is measured using a push rod resting on the upper end piece. The change in length of the assembly contains contributions due to the liquid volume expansion, as well as two correction terms, one each for the expansion of the enclosing hollow cylinder and the end pieces. The precision of expansivity data so obtained is  $\pm 3.5\%$ . The method was tested, using NIST SRM 710 standard soda-lime glass against the previously used method of combined dilatometry and calorimetry. Comparison of these two methods reveals a good agreement for the liquid expansivity. The agreement of the new and old methods supports the assumption built into the latter that volume and enthalpy relaxation follow identical kinetics in these silicate melts. The new method makes no assumptions regarding the relaxation processes of enthalpy and volume relaxation and opens up many further experimental possibilities including applications at higher pressures.

#### INTRODUCTION

The density of silicate liquids is a fundamental input into the derivation of buoyancy forces associated with melt transport in magmatic processes (Lange and Carmichael 1990). As such, the derivation of an adequate equation of state for the *PVT* properties of liquid silicates is an important experimental goal of petrology, geophysics, and geochemistry (Bottinga and Weill 1970; Bottinga et al. 1982). Considerable effort has therefore been invested in determining melt density as a function of composition, temperature, and pressure in the past decade. Several of these efforts have relied on traditional and widely accepted methods such as high-temperature immersion methods (e.g., Lange and Carmichael 1987; Dingwell and Brearley, 1988; Dingwell et al. 1988; Dingwell 1990) and both high-temperature and high-pressure Stokesian falling sphere techniques (Scarfe et al. 1987; Taniguchi 1989). Those methods are well suited to low viscosity melts ( $<10^3$  Pa s and  $<10^5$  Pa s, respectively). This, however, restricts their range of applicability to relatively basic melt compositions at relatively high temperatures. Recent development of dilatometric methods for the determination of density and thermal expansion of relaxed silicate liquids (Webb et al. 1992) is highly complementary to the above traditional methods and was used, for example to first obtain the temperature dependence of the expansivity of geologically relevant silicate melt compositions (Knoche et al.

1992a, 1992b, 1992c, 1994, 1995; Dingwell et al. 1993a, 1993b). The derivation of liquid expansivity from dilatometry is based on the testable assumption that the kinetic parameters controlling the relaxation of enthalpy and volume in the glass transition are equivalent and transferable. Although evidence was presented to support this assumption, its validity has been questioned. Several dilatometric investigations of silicate melts report relaxed density at or near the glass transition but did not include direct estimates of the liquid expansivity (Lange 1997a, 1997b; Ochs and Lange 1997). As a result, the methods used to obtain expansivity for silicate melts just above the glass transition and the data themselves are in dispute. Direct determination of liquid expansivity data just above the glass transition could potentially resolve this controversy. Unfortunately, push rod dilatometric systems operating on unconstrained cylinders of glass cannot yield such data because uncontrolled longitudinal sample deformation sets in at the glass transition. Sample containment however provides a practical solution to the exact measurement of total volume expansion above the glass transition, and in fact a “thermometer” style geometry of a semi-contained sample was employed by Fiske and Stebbins (1994) recently for liquid expansivity. For the first time ideas from Gottsmann et al. (1998) are demonstrated by direct determinations of the expansivity of a silicate liquid above the glass transition using container-based linear dilatometric techniques. For the standard glass investigated, comparison with our earlier dilatometric/calorimetric techniques, reveals good agreement for the derived values of liquid expansivity.

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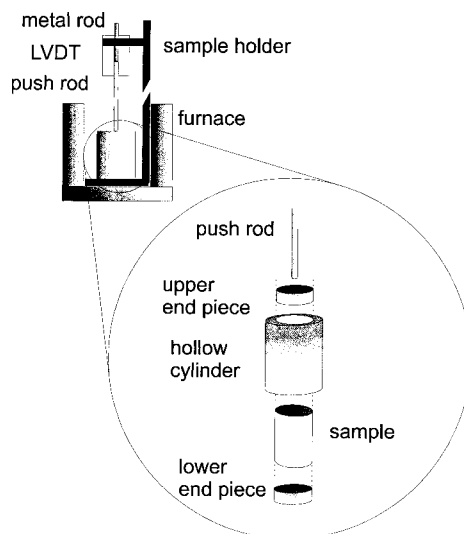
## EXPERIMENTAL METHODS

## Container-based dilatometry

A soda-lime silicate standard glass (NIST SRM 710) was chosen for several reasons. (1) It is viscometrically extremely well characterized, serving as a viscosity standard for rheological laboratories worldwide (including ours) and is widely available. This meant that the temperature of the glass transition was predictable. (2) The temperature of the glass transition is in a range where dilatometric and calorimetric access with high precision scanning systems is possible. (3) This melt composition was considered to be chemically inert enough to avoid chemical attack of the container metal used in this study. This has been confirmed during the present study via microprobe analyses of recovered glass products. (4) The relatively depolymerized composition of this soda lime silicate glass ensured that both the relaxational enthalpy and volume changes as well as the change in expansivity across the glass transition would be large and therefore provide the possibility of a precise test of the method and its comparison with the dilatometric/calorimetric technique. Its chemical analysis, reproduced from the National Bureau of Standards (1962) data sheet, is SiO<sub>2</sub> 70.5 wt%, Na<sub>2</sub>O 8.7 wt%, K<sub>2</sub>O 7.7 wt%, CaO 11.6 wt%, Sb<sub>2</sub>O<sub>3</sub> 1.1 wt%, SO<sub>3</sub> 0.2 wt%, R<sub>2</sub>O<sub>3</sub> 0.2 wt%, (Fe<sub>2</sub>O<sub>3</sub> 0.02 wt%).

Samples for dilatometry were carefully drilled from the original standard block as obtained from NIST using a diamond corer. These cores were then precisely cut to lengths of 14 mm to obtain right cylinders of 8 mm diameter. The ends of the drilled and cut cylinders were ground and polished to 1 μm fineness to ensure good contact with the container. Samples were then dried at 90 °C and stored in a desiccator.

The container (Fig. 1) consists of three separate pieces: one hollow right cylinder and two smaller solid cylindrical “end pieces.” The room temperature inner diameter matches precisely the outer diameter of the sample cylinder and its length is approximately 6 mm longer than that of the sample. The room temperature diameter of the end pieces matches that of the sample and their cumulative length is approximately 6 mm, the difference between the lengths of the sample and the hollow cylinder. The container and the end pieces are machined from 99.9 wt% Ni metal, whose coefficient of thermal expansion was precisely determined here using the same dilatometer. All surfaces of the



**FIGURE 1.** Schematic illustration of the container assembly used for the containment of liquid samples during the determination of their liquid thermal expansivity. The container is machined from Ni-metal. Its inner dimensions match precisely those of the ground and polished surface of the sample cylinder at room temperature. The upper end piece is free to move vertically and records as an assembly length change the combined expansion of the sample and the container as a function of temperature above the glass transition curve.

container that contact the sample were polished to ensure goodness of fit, which is crucial because cracks or voids could possibly lead to bubble development at high temperature. Glasses containing bubbles were discarded prior to dilatometry. We observed no bubble generation during dilatometry.

The linear thermal expansion of the container was measured by scanning runs in which the push rod of the dilatometer was placed on the upper surface (outer rim) of the container. Such determinations were carried out during the heating procedure up to 765 °C and during the cooling procedure to room temperature. These thermal expansivity data (Table 1) were incorporated in the corrections applied to assembly expansion data that are described next.

The dilatometer is a Netzsch TMA 402 Quartz-rod dilatometer in vertical geometry. The sample assembly is supported on

**TABLE 1.** Thermal properties of soda lime glass and its container

$T$ °C	$dV/dT^*$	$\Delta V/\Delta T$ $10^{-4} \text{ cm}^3/\text{mol}\cdot\text{K}$	$V^*$	$V$ $\text{cm}^3/\text{mol}$	$\alpha_v^*$	$\alpha_v$ $10^{-6}/\text{K}$	$\alpha_{Ni}$ $10^{-6}/\text{K}$
635*	$23.3 \pm 0.8^*$	—	$25.07 \pm 0.04^*$	—	$93.1 \pm 2.7^*$	—	—
640		$22.1 \pm 0.7$		$25.08 \pm 0.05$		$88.1 \pm 3.0$	$16.7 \pm 0.1$
670		$17.6 \pm 0.6$		$25.14 \pm 0.05$		$70.1 \pm 2.5$	$17.1 \pm 0.2$
700		$17.8 \pm 0.6$		$25.20 \pm 0.05$		$70.7 \pm 2.5$	$17.4 \pm 0.2$
730		$16.7 \pm 0.6$		$25.25 \pm 0.05$		$66.1 \pm 2.3$	$17.7 \pm 0.1$
754		$36.7 \pm 1.3$		$25.34 \pm 0.05$		$145.4 \pm 5.1$	$17.7 \pm 0.1$

*Note:* The volume expansivity ( $dV/dT$ ,  $\Delta V/\Delta T$ ), molar volume ( $V$ ), volume coefficient of thermal expansion ( $\alpha_v$ ) are of the NBS SRM 710 soda lime glass. The average linear coefficient of thermal expansion ( $\alpha_{Ni}$ ) is of the Ni-metal container and both end pieces within the supercooled liquid state. The container-based expansivity data is calculated over a temperature range of 30 K except the value for 640 °C where the temperature interval was 20 K. Therefore we refer to  $\Delta T/\Delta V$  rather than  $dV/dT$ . The average coefficient of volume thermal expansion using the container-based method was calculated from the expansivity data and the average of both volumes, defining the temperature interval  $\Delta T$ .  $\alpha_{Ni}$  was derived from scanning runs using the Netzsch TMA 402 dilatometer. The container was heated to 765 °C and successively cooled down with matching heating and cooling rates of 5 K/min. See text for details.

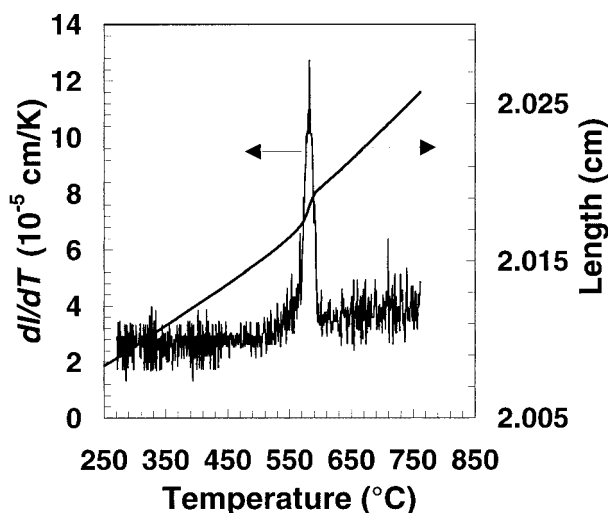
\* This is derived by the combination of volume and enthalpic relaxation using the method of Webb et al. (1992). All other values were obtained directly using the new container-based dilatometry.

a silica glass base connected to a measuring head above the sample. The push rod sits on the horizontal top side of the sample assembly and is also manufactured from silica glass. It is attached to a Vanadium metal rod by a thread closure. The Vanadium-rod runs through a vertically mounted linear variable displacement transducer (LVDT), which has been calibrated against standard single crystal corundum. The rod is supported by a spring, which is adjusted to minimize the force exerted by the rod weight on the upper surface of the sample. For additional details see Webb et al. (1992).

The sample assembly, consisting of the sample cylinder and container components, was loaded into the dilatometer at room temperature and heated at 5 K/min to temperatures up to 180 K above the observed glass transition temperature. We emphasize that the glass transition temperature is taken as the peak temperature value of the expansivity curve (Fig. 2).

### Unconstrained dilatometry

As a test and comparison, we used the previous dilatometric/calorimetric comparative technique to derive liquid expansivity values for the same sample melt. This method, described in full by Webb et al. (1992), is based on the principle of the equivalence of enthalpy and volume relaxation in silicate melts and involves (1) the determination of the specific heat capacity of the sample from room temperature up to 40–60 °C above the glass transition temperature; (2) the determination of the density of the sample at room temperature using an Archimedean technique; (3) the monitoring of the vertical elongation by dilatometry to obtain the thermal molar expansivity of the



**FIGURE 2.** A raw dilatometric trace of the assembly length change and a differentiated trace of the same signal as an expansivity, from an experiment where the glass sample is contained as described in Figure 1. Three domains are visible. The lower temperature domain describes glassy linear expansion. The glass transition interval expresses a hysteresis due to relaxation and the conversion from linear glassy data to liquid volume data. The higher temperature segment contains direct information on the linear expansivity of the contained liquid sample. All three segments must be corrected for the container contribution to thermal expansivity.

sample across the glass transition; (4) the normalization of both the calorimetric and the dilatometric data with the temperature-dependent glassy values equal to zero and the value at the peak of the individual curves equal to one; (5) the derivation of the liquid expansivity of the sample from the comparison of the two normalized data sets.

The samples were diamond cored (6 mm diameter) from the NIST SRM 710 glass block, cut to a length of 10 mm, and ground and polished to within 0.001 mm to ensure plain surfaces. The samples were dried at 90 °C and stored in a desiccator until their use in the experiment.

The samples are placed in platinum crucibles with geometries matching those of the samples for the calorimetric measurements. The specific heat capacities are determined using a differential scanning calorimeter (DSC 111, Setaram). The samples were heated at constant heating rates of 5 K/min across the glass transition interval to allow enthalpic relaxation but successively cooled at variable cooling rates of 10, 5, 2, and 1 K/min. Four measurements resulted from this thermal treatment runs. The calorimeter is calibrated against the heat capacity of a single crystal sapphire with matching geometries. The heat capacity data are taken from Robie et al. (1979). The precision of the heat capacities is  $\pm 1\%$  for the glassy values and  $\pm 2\%$  for the super cooled liquid values. The accuracy of the heat capacity of the glass is  $\pm 1\%$  and for the metastable liquid values  $\pm 3\%$ , respectively.

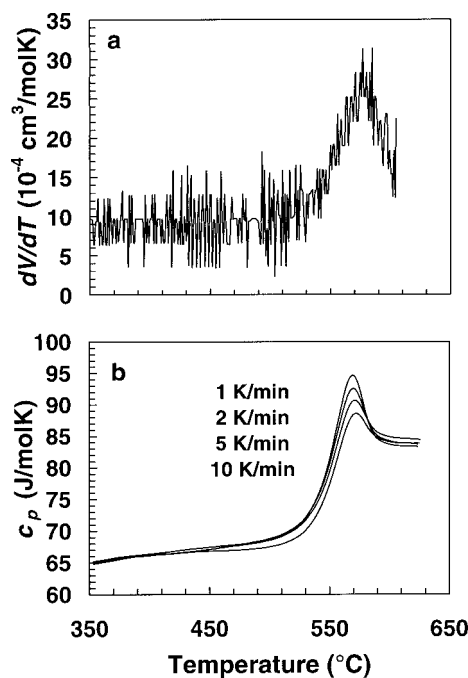
The density of the glass at room temperature was determined with the Archimedean buoyancy with ethanol and air. Additionally the sample density was calculated from the exact sample geometry involving the volume and mass of the glasses. Before the density determination, the glasses were cooled at a set cooling rate of 5 K/min to ensure precise comparison of the density measurements with the dilatometrically and calorimetrically obtained property values. The density of the glass (2.524 g/cm<sup>3</sup>) derived from both the buoyancy method and the geometrically calculated density matches within  $\pm 0.02\%$ .

For the dilatometric measurement the sample is placed inside the Netzsch TMA 402 vertical dilatometer and is heated at a constant rate of 5 K/min approximately 30 °C beyond the peak value temperature of the thermal expansion. Successively, the sample is cooled down at set cooling rates matching those of the calorimetric treatment before being reheated at 5 K/min. The dilatometer is calibrated against a standard single-crystal sapphire. This calibration together with the reproducibility due the thermal treatment runs results in an accuracy of  $\pm 2.5\%$  for the expansivity data.

The normalized calorimeter trace is applied to the dilatometric molar expansivity curve (Fig. 3) to extend it to the super-cooled liquid region and to calculate the thermal volume expansivity, volume, and coefficient of thermal volume expansion  $\alpha_v [1/V \cdot (dV/dT)]$ . Values are given in Table 1.

### RESULTS AND EVALUATION

The resulting container-based dilatometric trace (Fig. 2) clearly shows the glassy segment of the expansivity data, the glass transition region, and the super- $T_g$  segment of the trace. The length path of the glassy sample cylinder up to and through the glass transition follows a potentially complex sequence of events. Although the close fit of the glass cylinder to the metal



**FIGURE 3.** The dilatometric (a) and calorimetric (b) traces obtained for an unconstrained cylinder of the standard glass investigated here. These data have been evaluated using the methods of Webb et al. (1992) and a value of the liquid state volume expansivity of the melt has been derived. The values of expansivity derived from the combined dilatometric/calorimetric data illustrated here are in good agreement with values derived from the new method. (a) Shows the dilatometric trace of a sample at matching cooling and heating rates of 5 K/min. (b) Displays the  $C_p$ -traces of the sample after applying various cooling rates and subsequent reheating at 5 K/min.

cylinder at room temperature is essential for this experimental approach, the higher expansivity of the metal container with respect to the glass results in a compressive stress-free expansion of the glass up to the glass transition interval. Within the glass transition, the situation changes significantly because the sample expansivity exceeds the expansivity of the metal container. Although compressive stresses may occur they are however fully relaxed out as the sample crosses the glass transition and thus they need not concern us here unless they generate cracks in the glass cylinder. The signal in the hysteresis interval near the glass transition must also result from a relatively complex combination of effects. These include the relaxation of the glass volume controlled by the liquid viscosity, the minor flow of the melt within the enclosing geometry to obtain a fully wetted optimal geometry, and any geometrical considerations involved in transferring from the measurement of linear expansion of a solid body below  $T_g$  to the linear expression of the volume expansion of the liquid body above  $T_g$ . As such, the present method is entirely free of assumptions regarding the relaxational behavior of the melt except to state that the melt is fully relaxed above the glass transition. This is a powerful simplification.

At temperatures above the glass transition, the sample has adopted its relaxed volume in metastable equilibrium with the

ambient temperature and contains no memory of the thermal path that led it to its present high temperature.

In the following discussion, the subscripts  $T_0$ ,  $T_1$ , and  $T_x$  refer to parameter values at room temperature, at the temperature where the viscosity is  $10^6$  Pa s, and to any temperature within the super-cooled liquid state, respectively. The correction for the container expansivity is composed of two elements, one for the contribution of the end pieces to the total elongational dilatometric signal and one for the radial expansion of the volume available to the sample as defined by the hollow cylinder expansion.

Precise knowledge of the sample geometry inside the container at a temperature  $T_1$  (in our case  $757^\circ\text{C}$ ) can be used to quantify the molar volume of the sample. At this temperature the sample completely wets the container walls (see below). Thus the molar volume can be calculated from the elongational signal at that specific temperature and the area expansion of the base of the metal container by

$$V_{T_1} = l_1 \times A_{T_0} \times (1 + 2\alpha_{Ni} \times \Delta T) \times \frac{gfw}{\rho \times V_{T_0}} \quad (1)$$

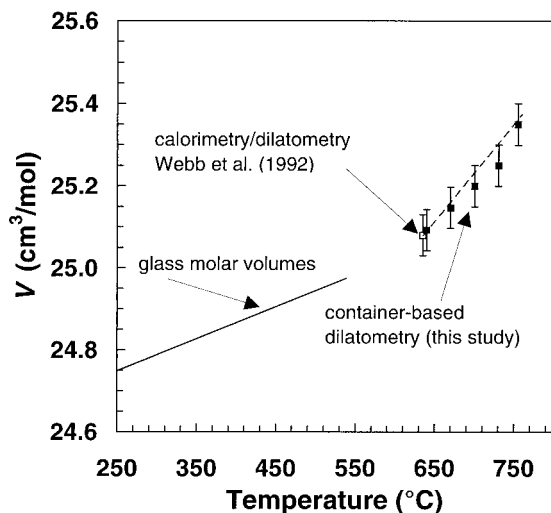
where  $l_1$  is the length of the sample at  $T_1$  derived from the total elongational signal of the assembly from which the elongational contribution of the two metal end pieces has to be subtracted.  $A_{T_0}$  is the base area of the sample which exactly matches the inner base area of the hollow cylinder at room temperature,  $\alpha_{Ni}$  is the average coefficient of linear thermal expansion of the Ni-container at  $T_1$ ,  $\Delta T$  is  $(T_1 - T_0)$ ,  $gfw$  is the gram formula weight in grams of the sample,  $\rho$  is the room temperature density of the sample, and  $V_{T_0}$  is the molar volume at room temperature.

Due to the higher expansivity of the metal container, we are not able to exactly quantify the sample geometry and thus its volume at any elevated temperature above  $T_g$  during the heating procedure as the sample will exhibit a longitudinal deformation. Therefore our dilatometric signal in the interval also consists of a concealed viscous deformation due to gravity that is not quantified. To calculate thermal expansivities within the super-cooled liquid state we refer instead to the dilatometric data obtained during the cooling procedure at a cooling rate of 5 K/min. The volume of the sample is precisely known at a temperature of  $757^\circ\text{C}$  (where  $\eta = 10^6$  Pa s; NIST data sheet) due to its wetting to the container walls. As a check on container wetting a dilatometric experiment was carried out, where a constrained NBS SRM 710 sample with an identical container assembly, geometry, and thermal history as the samples used in this study was heated at 5 K/min to a temperature of  $757^\circ\text{C}$  and was allowed to equilibrate for 30 minutes inside the container assemblage. The calculated molar volume of the equilibrated melt at  $757^\circ\text{C}$  is consistent to the volume derived from the pure scanning procedure to within  $\pm 0.2\%$ .

Consequently cooling down from  $757^\circ\text{C}$  the container walls remains wetted. Therefore we can calculate the molar volume of the sample at any temperature  $T_x$  within the relaxed super-cooled liquid state via

$$V_{T_x} = l_{x1} \times A_{T_0} \times (1 + 2\alpha_{Ni} \times \Delta T) \times \frac{gfw}{\rho \times V_{T_0}} \quad (2)$$

with  $l_x$  being the length of the sample at  $T_x$  corrected for the



**FIGURE 4.** Comparison of the derived expansivity data for contained and unconstrained samples using the new method (this study, solid squares) and the combined dilatometric/calorimetric method of Webb et al. (1992) (open square and dashed line). The molar volumes obtained by the new method are based on the dilatometric data derived from the cooling procedure of the assembly with a constant cooling rate of 5 K/min. Upon cooling the container walls are fully wetted allowing the direct determination of the sample volume at any temperature within the super-cooled liquid state.

contributions of the two metal end pieces. The thermal volume expansivity is calculated over a temperature interval  $\Delta T$  using

$$\frac{\Delta V}{\Delta T} = \frac{V_{T_x'} - V_{T_x}}{T_x' - T_x} \quad (3)$$

with  $T_x' > T_x$ . To calculate the average coefficient of volume thermal expansion the combination of Equations 2 and 3 gives

$$\alpha_v = \frac{\Delta V}{V_{\text{avg}} \times \Delta T} \quad (4)$$

with  $V_{\text{avg}}$  being the average of both volumes, defining the temperature interval  $\Delta T$ .

Figure 4 illustrates the results obtained for volume vs. temperature using both the new container-based method and the old dilatometric/calorimetric comparative method. The results can be seen to be in good agreement demonstrating that the assumptions built into the older method of Webb et al. (1992) are completely satisfactory. Nevertheless, the present method is entirely free of assumptions regarding the relaxation behavior of the samples and therefore is to be recommended in future liquid expansivity studies. Potential further applications of a container-based approach include expansivity and phase change studies at high temperatures and under elevated pressures in internally heated gas vessels (Gennaro et al. 1998).

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