Determination of the limiting fictive temperature of silicate glasses from calorimetric and dilatometric methods: Application to low-temperature liquid volume measurements

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ABSTRACT

The limiting fictive temperatures (T’ f) of 16 multi-component silicate glasses have been derived quantitatively from heat capacity measurements, following the method of Moynihan et al. (1976). These quantitative values of T’ f closely match temperatures corresponding to the onset (T onset) of the rapid rise in dilatometry heating curves (dL/L vs. T) at the glass transition, obtained on glasses with similar cooling histories. The mean deviation (T’ f – T onset) is 5 K, whereas the maximum deviation is 17 K. These results confirm that the T’ f of a silicate glass can be determined from the T onset of a glass dilatometry curve with an uncertainty that is <20 K. An application of the T’ f measurements includes the precise determination of the specific volumes of supercooled liquids at their respective T’ f values (Lange 1997). By comparison with other measurements in the literature, the accuracy of the T’ f method for determining low-temperature, fully relaxed, supercooled liquid volumes is shown. A comparison of volume-temperature models in the literature shows that a linear model (where thermal expansivity is independent of temperature) provides a superior fit of measured volumes in the SiO2-Al2O3-MgO-CaO-Na2O-K2O system over very wide temperature intervals (700–1900 K).

INTRODUCTION

Although magmatic processes occur over a considerable range of temperature and pressure conditions, experimental measurements of melt properties generally can only be performed over a limited temperature and pressure range. For example, direct density measurements of silicate liquids utilizing the double-bob Archimedean method are restricted to liquids that have viscosities less than 107 Pa-s, which prevents measurements at low temperatures near the glass transition. In addition, high-quality density measurements are difficult to make on liquids under high-pressure conditions, which severely limits measurement on melts with substantial amounts of dissolved water because of problems with devolatilization (an exception is Burnham and Davis 1971).

This gap in the density data set has been partially relieved by determining the volume of anhydrous (Knoche et al. 1992, 1995; Lange 1996, 1997; Gottsmann and Dingwell 2000; Toplis and Richet 2000) and hydrous (Ochs and Lange 1997, 1999) silicate liquids near the glass-transition. The method employed by Lange (1996, 1997) and Ochs and Lange (1997, 1999) differs from the other studies cited above in that it does not involve measurements of thermal expansivity into the glass-transition interval, but instead requires the determination of the limiting fictive temperature (T’ f) of glasses, as detailed below.

Measurements of liquid volumes at T’ f (for 24 different samples) currently forms the basis of a linear volume-temperature model for SiO2-Al2O3-MgO-CaO-Na2O-K2O liquids (Lange 1997), which is calibrated on a data set that ranges from 701 to 1896 K. The success of that model (detailed below) suggests that the thermal expansivity of experimental liquids can be considered temperature-independent for all practical applications. Exceptions are Fe3+ and Ti4+-bearing alkali silicate liquids (Lange et al. 1998; Liu and Lange 2001), which also show temperature-dependent heat capacity behavior (Richet and Bottinga 1982; Lange and Navrotsky 1993; Tangeman and Lange 1998). Recently, however, a controversy has emerged over whether the thermal expansivity of silicate liquids is strongly temperature-dependent, with a focus on diopside liquid (Knoche et al. 1992; Lange 1997; Gottsmann and Dingwell 2000; Toplis and Richet 2000; Lange 2001). In light of this controversy, it is important to establish not only that T’ f values can be approximated accurately, but also that the T’ f method for determining low-temperature liquid volumes is accurate and consistent with the results from other techniques used in different laboratories.

The purpose of this study is therefore fourfold. First, we establish the accuracy of T onset (the onset of the rapid rise in a dilatometry curve at the glass transition) as an approximation of the true value of T’ f. This is achieved by comparing T onset values derived from dilatometry heating curves to values of T’ f obtained quantitatively, following the method of Moynihan et al. (1976). Second, we illustrate the effects of structural relaxation on the room-temperature density of the glasses, as well as on the shape and temperature interval of the glass-transition on calorimetry and dilatometry curves. Third, we show that the low-temperature volume measurement of Lange (1997) on diopside (CaMgSi2O6) liquid, based on the T’ f method, is in excellent agreement with similar low-temperature measurements made on diopside liquid by slightly different methods (e.g., Gottsmann and Dingwell 2000; Toplis and Richet 2000). Fourth, we demonstrate that a linear volume-temperature model,