INTRODUCTION

Water is, without a doubt, the most important volatile component in Earth’s crust and mantle, and its presence can substantially alter physical and chemical properties of silicate melts including the viscosity, through the depolymerisation of the melt (Burnham 1979). Water is incorporated into silicate melts as both \( \text{OH} \) groups and molecular \( \text{H}_2\text{O} \) according to the reaction

\[
\text{H}_2\text{O}_{\text{melt}} + \text{O}_{\text{melt}} \rightarrow 2\text{OH}_{\text{melt}} \tag{1}
\]

(Stolper 1982a, 1982b; also see review by McMillan 1994). Previous work was performed on silicate glasses quenched from melts, assuming that the speciation in the glass reflected that of the melt at the temperature from which it was quenched (Stolper 1982a). However, Dingwell and Webb (1990) showed that this assumption is incorrect because the relaxation rates in silicate melts above the glass transition temperature \( T_g \) are so fast that the water speciation cannot be quenched from temperatures above \( T_g \). These authors proposed that the speciation recorded in the glass reflects the equilibrium at the bulk \( T_g \) for the system.

Recent advances allow in-situ study of silicate melts and glasses at both temperature and pressure. Specifically, Keppler and Bagdassarov (1993) measured IR spectra of a rhyolite containing 300 ppm water to 1300 °C, and observed changes in the type of \( \text{OH} \) groups present below the bulk \( T_g \) of the system. Nowak (1995), Nowak and Behrens (1995) and Shen and Keppler (1995) reported speciation measurements on silicate glasses at both high temperature and pressure, and found that the speciation did change below \( T_g \). However, Behrens et al. (1998) and Withers and Behrens (in preparation) disagreed with these conclusions, and instead postulated that the changes in band intensities were due to changes in the molar absorption coefficients with temperature. The studies of Shen and Keppler (1995), Nowak (1995), and Nowak and Behrens (1995) have also provided information on the thermodynamics of the reaction obtained from the equilibrium constant for the speciation reaction. Previous studies concentrated on simple analogue systems such as albite or haplogranite, but few in-situ water speciation studies have been performed on compositions found in nature (Withers et al. 1998; Withers and Behrens, in preparation). Here we present in-situ results from a series of synthetic compositions close to natural rhyolite.

EXPERIMENTAL METHOD

Sample synthesis and preparation

An anhydrous “average” rhyolite glass was prepared from a mixture of \( \text{SiO}_2 \), \( \text{Al}_2\text{O}_3 \), \( \text{MgO} \), \( \text{CaCO}_3 \), \( \text{Na}_2\text{CO}_3 \), \( \text{K}_2\text{CO}_3 \) by heating first to 1200 °C for 24 hours to decarbonate the starting materials then melting at 1600 °C in a Pt crucible for one hour. Microprobe analysis obtained at 15 kV, 10 nA, using a 30 µm spot size gave a total of 98.36 with \( \text{SiO}_2 = 74.13, \text{Al}_2\text{O}_3 = 13.92, \text{K}_2\text{O} = 5.24, \text{Na}_2\text{O} = 2.90, \text{CaO} = 1.16, \text{MgO} = 1.01 \text{wt\%}. \) No Fe