The effect of coordination changes on the bulk moduli of amorphous silicates: The SiO$_2$-TiO$_2$ system as a test case

QUENTIN WILLIAMS$^{1,*}$, MURLI H. MANGHANI$^2$, AND TERUYUKI MATSUI$^3$

$^1$Department of Earth and Planetary Sciences, University of California, Santa Cruz, California 95064, U.S.A. Orcid 0000-0002-4798-5578
$^2$Hawaii Institute of Geophysics & Planetology, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.
$^3$Knowledge Outsourcing Co., Inc, Nagoya, Japan

ABSTRACT

The elasticity of a sequence of SiO$_2$-TiO$_2$ glasses is examined at high pressures and temperatures. A primary goal is to determine how the previously proposed substitution of fivefold-coordinated Ti at low concentrations of Ti and fourfold-coordinated Ti at higher concentrations affects the elastic properties of these glasses. The effect of changing Ti content on the bulk moduli of these glasses is monotonic, and no systematic effect of possible coordination changes is observed. In contrast, there is an apparent decrease in the pressure derivative of the bulk modulus above ~3 wt% TiO$_2$. This change occurs at a similar composition to that at which a transition from predominantly fivefold to fourfold of Ti has been proposed to occur in these glasses. Hence, this shift in the pressure derivative of the bulk modulus is attributed to a stiffening of the equation of state of these glasses generated by the substitution of fivefold Ti species relative to TiO$_2$ units. Our results provide rationales for the onset of coordination changes producing a minimal change in the equation of state of silicate melts/glasses, and for bulk moduli determined at ambient pressure producing relatively accurate silicate melt volumes even within liquids that have begun to undergo coordination changes. Thus, our results support the general validity of single equation of state formulations that describe the densities of silicate melts through the transition zone and shallow lower mantle.

Keywords: Glasses, elasticity, ultrasonics, coordination changes, polymerized silicates

INTRODUCTION

The densities of silicate melts at high pressures are of pivotal importance for a range of geophysical issues involving the differentiation and chemical evolution of the Earth. Densities of silicate melts at high pressures govern whether melts rise or sink at depth, with associated upward or downward transport of incompatible elements. And, the relationship between the pressure dependence of the densities of melts and the shape of the melting curves of materials plays, via the Clausius-Clapeyron equation, a pivotal role in determining how magma oceans solidify (e.g., Andrault et al. 2011; Boukare et al. 2015). The densification of silicate melts at depth within Earth’s transition zone and shallow upper mantle has long been recognized to hinge on coordination changes within network-forming components such as Si and Al, from fourfold to higher coordinations (e.g., Waff 1975; Williams and Jeanloz 1988; Yarger et al. 1995; Farber and Williams 1996; Stixrude and Karki 2005). Despite these now well-documented coordination changes under pressure, the elastic properties of melts measured at ambient or low pressures (in a pressure range where few highly coordinated Si and Al atoms are anticipated to be present (e.g., Xue et al. 1991; Allwardt et al. 2005) are in fairly good accord with the densities of liquids at conditions under which coordination changes almost certainly have begun to occur within liquids. Specifically, the compaction of silicate liquids under either static or shock loading into pressure ranges of tens of gigapascals (e.g., Rigden et al. 1989; Miller et al. 1991; Asimow and Ahrens 2010; Thomas et al. 2012; Sanloup et al. 2013)—a range that is associated with coordination changes (typically, from four- to five- or sixfold) of network-forming cations within the liquid structure—is, perhaps counter-intuitively, reasonably well predicted from ambient-pressure ultrasonic data on silicate liquids, which show that silicate liquids have typical ambient pressure bulk moduli of 17–23 GPa (e.g., Manghnani et al. 1986; Rivers and Carmichael 1987; Secco et al. 1991; Ai and Lange 2008). This similarity raises the fundamental question: what is the effect of highly coordinated species on the elasticity of silicate liquids in particular and amorphous silicates in general?

A straightforward means of evaluating the precise effect of coordination changes on the elastic behavior of amorphous silicates involves making accurate elastic measurements on a simple system in which a shift in coordination is well documented. Previous measurements of elasticity of glasses under pressure (e.g., Sanchez-Valle and Bass 2010; Liu and Lin 2014) have not readily constrained the precise interplay between complex, ill-constrained shifts in coordination (e.g., Fukui and Hiraoka 2018) and elasticity. In contrast to the multiple coordination environments likely to be generated under compression, relatively well-characterized changes in coordination induced by compositional changes at ambient pressures can illuminate the degree to which a direct connection exists between structural and elastic changes. In particular, titanium substitution in silica provides a test case with which to understand this issue of primary geophysical relevance: X-ray absorption near edge