The role of modifier cations in network cation coordination increases with pressure in aluminosilicate glasses and melts from 1 to 3 GPa

SAURAV BISTA1,* AND JONATHAN F. STEBBINS1

1Department of Geological Sciences, Stanford University, Stanford, California 94305, U.S.A.

ABSTRACT

Previous studies have shown that both NBO content and modifier cation field strength play important roles in increasing the network cation coordination with increasing pressure. It has been observed in previous studies that the increase in average Al coordination with pressure in alkali aluminosilicates depends on NBO concentration, where large increases in Al coordination with pressure have been observed for compositions containing significant concentrations of NBO and little or no Al coordination increase observed in glasses containing negligible NBO at pressures ranging from 1 to 3 GPa. Similarly, in NBO rich aluminosilicates and aluminoborosilicates containing different modifier cations, it was reported that the increase in average Al coordination followed a steeper rise with increasing pressure in compositions containing higher field strength modifiers. In this study, we look at Ca- and Mg-aluminosilicate glasses across all three compositional regimes (peralkaline, metaluminous, and peraluminous) to study the effect of both oxygen speciation and modifier cation field strength on network cation coordination changes with pressure. Our study shows that in Mg aluminosilicate glasses (both peralkaline and metaluminous), the increase in average Al coordination can be quite large and show no significant impact from differences in oxygen speciation (NBO content). In contrast, in Ca-aluminosilicate glasses, the oxygen speciation has a notable impact with the average Al coordination following a steeper rise with increasing pressure in a peralkaline composition and less steep for a metaluminous composition.

Keywords: High pressure, glasses and melts, NMR spectroscopy, aluminum coordination, non-bridging oxygen, cation field strength, densification, aluminosilicate

INTRODUCTION

The properties of melts and glasses at high pressure are significantly different from those at ambient pressure, and such changes, as well as their structural causes, are important for geological processes as well as technological applications (Striepe et al. 2013; Januchta et al. 2017). In aluminosilicate melts, the changes in aluminum structural environment with increasing pressure have been widely studied through $^{27}$Al MAS NMR studies on glasses that are quenched from high temperatures at high pressure and decompressed to ambient pressure (Yarger et al. 1995; Allwardt et al. 2005a; Kelsey et al. 2009b; Lee et al. 2012). Significant coordination increases have been recorded with this approach. Recent studies have also shown, however, that large transient-pressure drops may occur during quench from high temperatures in solid-media apparatus, and that resulting data may actually significantly underestimate structural changes (Bista et al. 2015). More accurate recording of the actual quench pressure, and resulting structural changes, can be made in experiments conducted near the glass transition temperature ($T_g$). Near to $T_g$, the structure can relax to that of the metastable, supercooled liquid within seconds or minutes, without the need for subsequent substantial cooling to quench in the structure, which can be accompanied by significant pressure drop caused by thermal contraction.

It is important to note that in situ experiments at high pressure and temperature would be ideal to completely characterize the pressure effects on structure, but as yet are not feasible to observe the detailed changes measurable by NMR on recovered, decompressed glasses. In situ Raman spectroscopic studies of silicate melts and glasses at high pressure have shown some evidence that the structure of decompressed glasses can be different from those at high pressure (Wolf et al. 1990; Farber and Williams 1996), particularly at very high pressures where all network cations have increased coordination numbers. Our previous studies of the effect of decompression rates on recovered structural changes from high pressure (Allwardt et al. 2004, 2005b) also point to possible effect of decompression on ex-situ analysis of the recovered glass. Some aspects of structural relaxation may occur more readily upon decompression (e.g., elastic compression of O atoms around weakly bonded modifier cations and distortion of network cation polyhedra) while others might be expected to change more slowly on decompression at ambient $T$ (e.g., those involving breaking strong network bonds such as Si, Al, and B coordination). It is clear that in the range of pressure and densification studied here, large changes in network cation coordination, network bond angle distribution, and even some changes in modifier cation coordination are retained (Kelsey et al. 2009b), which record major effects of composition and that are correlated with measured, recovered density increases. In one unique study (Malfait et al. 2014), measurements of elastic...