LETTER

An in situ high-pressure NMR study of sodium coordination environment compressibility in albite glass

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ABSTRACT

The pressure-dependent modification of the Na-O coordination environment in albite glass is studied in situ to 2 GPa using high-pressure solid-state 23Na nuclear magnetic resonance spectroscopy. Compression of the glass at ambient-temperature results in shortening of the Na-O bond distance. The concomitant decrease in volume of the local Na-O coordination environment alone can account for the bulk compressibility of albite glass at 300 K. These results provide the first direct experimental evidence of a collapse of the open aluminosilicate framework that helps explain previously reported densification of aluminosilicate glasses and liquids at relatively low pressures without accompanying change in the average coordination number of the network forming Al and Si cations. Such structural changes at relatively low pressures may have far reaching implications for the mechanistic understanding of compressibility and viscosity anomalies characteristic of open tetrahedral aluminosilicate network glasses and melts of geological importance.

Keywords: In situ, high pressure, NMR, glass structure, compressibility, albite, sodium aluminosilicate

INTRODUCTION

The physical properties of vitreous and molten NaAlSi3O8 (hereafter referred to as albite) have been studied extensively as an analog for strongly polymerized melts generated and differentiated in the Earth’s crust. Although the thermal expansion, compressibility, and viscosity of albite glass/liquid at 1 atm conditions are relatively well constrained (e.g., Kress et al. 1988; Lange 1996; Sipp et al. 2001), one must extrapolate these physical properties to higher pressures to model the magmatic processes that occur within the Earth. Accurate predictions of silicate melt properties at pressure depend on detailed understanding of the structural changes accompanying their densification.

Albite, like silica, is a fully connected three-dimensional network of corner-shared [AlO4]4- and [SiO4]4- tetrahedra. Much like silica, but with (Na+ + Al3+) substituted for ⅔ of the Si4+, albite glass at 1 atm maintains an open framework structure. Na+ cations occupy the large holes within the aluminosilicate framework and charge-compensate for the negatively charged [AlO4]4- tetrahedra (Lee and Stebbins 1999, 2000). Both albite and silica glass are highly compressible, and become more compressible with increasing pressure below ~2.5 GPa (Bridgman et al. 1925; Kuryaeva and Surkov 2010; Sonnevile et al. 2013). This behavior is considered to be anomalous as it is the opposite of what is expected and observed for crystals with the same chemistry (Bensusa et al. 2005).

While the changes in the density of albite and silica glass are large within the first few GPa of compression, the concomitant structural changes of the coordination environments of the network-forming cations are found to be subtle. X-ray diffraction (XRD) studies of albite glass structure recovered from pressures <2.0 GPa identify only minor distortions of the tetrahedral network (Hochella and Brown 1985). On the other hand, samples synthesized at relatively high pressures >6 GPa show shortening of both the Na-O (Lee et al. 2006) and T-O (T = Si,Al) bond distances, reduction of the intertetrahedral bond angles <T-O-T> (Stebbins and Sykes 1990; Sykes et al. 1993) and the presence of some Al coordinated by >4 O atoms (Yarger et al. 1995; Allwardt et al. 2005). The lack of major changes to glass structure at low pressure forced these studies to speculate that the shortening of the Na-O bond distance must be the dominant mechanism of densification, similar to what is observed in perovskites with organic charge-balancing cations (e.g., Swainson et al. 2007), and indicative of a collapse of the open tetrahedral framework in the region of anomalous compressibility, as mentioned above. However, this hypothesis lacks direct experimental confirmation because such pressure-induced topological changes are either partially or fully reversible on decompression making the evaluation of their true nature and extent impossible for ex situ structural studies. Observation of nearest-neighbor structural changes associated with elastic deformation requires application of an element-specific spectroscopic technique such as nuclear magnetic resonance (NMR) spectroscopy. The application of solid-state NMR spectroscopy in situ at high pressure is limited owing to the technological challenges associated with designing a high-pressure probe head (1) having suitable non-magnetic materials that can operate up to a few GPa, and (2) provides sufficient sensitivity and sample volume. Recently, we devel-