Constraining $^{17}$O and $^{27}$Al NMR spectra of high-pressure crystals and glasses: New data for jadeite, pyrope, grossular, and mullite

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ABSTRACT

The $^{17}$O NMR spectra of glasses quenched from melts at high pressure are often difficult to interpret due to overlapping peaks and lack of crystalline model compounds. High-pressure aluminosilicate glasses often contain significant amounts of $^{[5]}$Al and $^{[6]}$Al, thus these high-pressure glasses must contain oxygen bonded to high-coordinated aluminum. The $^{17}$O NMR parameters for the minerals jadeite, pyrope, grossular, and mullite are presented to assist interpretation of glass spectra and to help test quantum chemical calculations. The $^{17}$O NMR parameters for jadeite and grossular support previous peak assignments of oxygen bonded to Si and high-coordinated Al in high-pressure glasses as well as quantum chemical calculations. The oxygen tricluster in mullite is very similar to the previously observed tricluster in grossite (CaAl$_2$O$_4$) and suspected triclusters in glasses. We also present $^{27}$Al NMR spectra for pyrope, grossular, and mullite.

Keywords: NMR spectroscopy, pyrope, grossular, mullite, jadeite, aluminosilicate glasses, oxygen-17, aluminum-27

INTRODUCTION

Structural studies of high-pressure aluminosilicate liquids and glasses are crucial for understanding natural magmas. In particular, it is important to ascertain how the network forming cations in these melts undergo increases in coordination number. $^{17}$O NMR directly studies the environment around oxygen atoms and can provide information on cation ordering as well as mechanisms for coordination number increases, complementing more direct observations of cation coordination by $^{26}$Si, $^{27}$Al NMR, and other methods (Lee and Stebbins 2000; Lee et al. 2003; Allwardt et al. 2004, 2005). The $^{17}$O NMR spectra of high-pressure aluminosilicate glasses often contain overlapping peaks and knowledge of NMR parameters for oxide ions in varying structural environments is essential to their interpretation. Quantum chemical calculations have been used to calculate $^{17}$O NMR parameters and assist in the assignment of peak positions to structural units (Xue and Kanzaki 1999; Lee et al. 2003; Lee 2004), but experimental studies of materials with known structures are still needed to test the validity of the calculated data. Crystalline phases often have well defined NMR line shapes and structures determined from X-ray diffraction, which allows NMR parameters to be matched to specific structural units, aiding the interpretation of NMR spectra of high-pressure glasses. This has been reliably used to determine $^{17}$O NMR parameters in alkali and alkaline-earth silicates to aid peak assignment in silicate glasses (Xue et al. 1994; Ashbrook et al. 1999, 2001, 2002, 2003; Loeser et al. 2003; Allwardt et al. 2004).

Recent studies of aluminosilicate glasses quenched from melts at pressures to 10 GPa have shown that most or all Si remains in four coordination, but substantial fractions of $^{[5]}$Al and $^{[6]}$Al are formed (Yarger et al. 1995; Allwardt et al. 2005). However, because crystalline phases containing $^{[5]}$Al are very few in number and generally have rather complex structures, we concentrate here on minerals containing $^{[6]}$Al. $^{[5]}$Al is dominant over $^{[6]}$Al in most high-pressure glasses, and the oxygen environment of these minerals will not be identical to the oxygen environment in high-pressure glasses. However, the NMR parameters from this study will be a useful step in understanding such systems. Thus far, the $^{17}$O NMR parameters have been determined for only a few $^{[6]}$Al containing minerals, e.g., kaolinite and muscovite (Lee and Stebbins 2003). The minerals in this study, jadeite (Na$^{[6]}$Al$^{[6]}$Si$_2$O$_6$), grossular (Ca$^{[6]}$Al$_4$Si$_2$O$_{12}$), pyrope (Mg$^{[6]}$Al$^{[6]}$Si$_2$O$_{12}$), and mullite (1.4$^{[4,6]}$Al$_2$O$_3$·1$^{[4]}$SiO$_2$ and 1.7$^{[4,6]}$Al$_2$O$_3$·1$^{[4]}$SiO$_2$), were chosen because they each contain oxygen bonded to $^{[6]}$Al with various common modifier cations. Their structures are also relatively simple and thus allow straightforward interpretation of $^{17}$O NMR spectra.

$^{27}$Al NMR can be used to directly observe and quantify the coordination of aluminum in high-pressure glasses (Allwardt et al. 2005). Model compounds are also needed to better understand and interpret $^{27}$Al NMR spectra of high-pressure aluminosilicate glasses. The $^{27}$Al NMR chemical shift for pyrope (1.8 ppm, Geiger et al. 1992 and 2.8 ppm, McMillan et al. 1989) and the $^{27}$Al for grossular (3.609 MHz, Derighetti and Ghose 1969) have previously been determined, however as we are currently able to conduct experiments using spectrometers in higher magnetic fields, it is useful to confirm and add to previous results. For completeness, we also present the $^{27}$Al NMR parameters for pyrope and grossular, and the $^{27}$Al MAS NMR spectra for mullite.

Mullite was also chosen for study because it contains the unusual structural unit of tetrahedral triclusters, three tetrahedra...