29Si CPMAS NMR investigations of silanol-group minerals and hydrous aluminosilicate glasses

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ABSTRACT

One-pulse magic angle spinning (MAS) 29Si and 1H-29Si cross-polarization (CP) MAS nuclear magnetic resonance (NMR) spectroscopy was performed on minerals with OH groups and on hydrous aluminosilicate glass samples. The silanol-group samples used were krauskopfite, rosenhahnite, thaumasite, ussingite, and KHSi2O5 with known Si to H distances and ellenbergerite, the proton positions of which are not as well defined. The Si-H distances from the minerals can be compared with the cross-polarization time constants (t_{SiH}) and the proton spin-relaxation times in the rotating frame [\tau_1(H)], and a rough correspondence exists between a mineral’s shortest Si-H distance and its t_{SiH} value. Also, fast [\tau_1(H)] values correspond to large bulk H densities. The CP spectra of the hydrous aluminosilicate glass samples were fitted with two peaks, representing two different Si environments within the glass structure. The contact-time curves of the higher frequency peak imply t_{SiH} similar to the mineral samples with short Si-H distances, and this suggests that the glasses could contain a large fraction of either Si-OH groups or protonated bridging O atoms.

INTRODUCTION

Water is the most abundant volatile in many terrestrial magmas, and it has a profound influence on their transport properties, such as viscosity, electrical conductivity, and cation diffusion rates. In one of the first models for water dissolution in aluminosilicate melts, Burnham (1975) suggested that water attacks the aluminosilicate framework, and tetrahedral bonds break to form Si-OH or Al-OH groups. Such depolymerization of the hydrous melt structure could explain observed decreases in viscosity. Later, a different model based on NMR spectroscopy was introduced by Kohn et al. (1989) proposing the exchange of H+ ions in the water with the Na+ ions of the melt as the main mechanism for water dissolution in aluminosilicate melts. In this model, no network oxygen bonds are broken, although the framework O atoms may be protonated. Despite numerous studies of hydrous aluminosilicate glasses some basic structural questions remain unanswered. Commonly, glasses have been studied as models for melt structures, because they represent the quenched-in structure of the melt at the glass transition temperature.

The mechanism of water solubility in aluminosilicate glasses has been studied extensively with techniques such as infrared spectroscopy and 1H, 17O, 23Na, 27Al, and 29Si NMR, and these experiments show that water is present as both H2O and OH (Stolper 1982; Eckert et al. 1988; Xu et al. 1998). A series of detailed NMR studies of aluminosilicate glasses (Kohn et al. 1989, 1998; Schmidt et al. 1999) have shown that the largest effects of added H2O is on the 23Na spectra, with relatively minor effects on the 29Si and 27Al spectra, leading to the conclusion that most OH groups are bonded to Na. However, the lack of detailed NMR studies of crystalline silicates containing OH has hampered the detailed interpretation of these and other data.

The present work uses 29Si magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) and 1H-29Si cross-polarization (CP) MAS NMR experiments to examine silanol groups in mineral structures, and explores the structure of hydrous glasses with albite (NaAlSi3O8) and haplogranite (NaAlSi3O6-KAlSi3O8-SiO2) compositions using the mineral data. The comparisons of the hydrous glass NMR parameters to the mineral NMR parameters allow inference of the Si-H distances.

CPMAS has long been used to improve NMR sensitivity and to help determine structural connectivity (Pines et al. 1973) and can produce information about inter-atomic distances, interactions and environments within solids. During a CPMAS NMR experiment the detected magnetization is generated by polarization transfer from a second nuclide (most commonly 1H). The sensitivity enhancement of the “rare spin” (e.g., 13C or 29Si) due to both the polarization transfer and the shorter proton relaxation times enables faster pulse repetition rates. 1H-13C CPMAS NMR is used routinely for organic solids (Engelhardt and Michel 1987). 1H-29Si CPMAS NMR, however, has found fewer applications.

CPMAS study, a series of experiments is often done with varying “contact times”, during which magnetization transfer occurs. The observed signal increases in intensity with a