Effects of intermediate range structure on the $^{29}$Si NMR chemical shifts of framework silicates: Results for analcime

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ABSTRACT

Seven natural analcime samples with atomic Si/Al ratios from 1.97 to 2.63 were investigated to explore the effects of intermediate range structure and Al for Si substitution up to the fourth nearest neighbor coordination shell on the $^{29}$Si NMR chemical shifts in the framework aluminosilicates. With increasing bulk Si/Al ratio, the $^{29}$Si chemical shifts of all Si(nAl) resonances become more negative (more shielded), consistent with previously reported trends for faujasite and LTA zeolite (Newsam 1985). For our analcimes, the total observed changes in chemical shift for the Si(3Al), Si(2Al), and Si(1Al) sites are ~0.5, 0.6, and 1.1 ppm, respectively, demonstrating that the effect of Si/Al ratio is more significant for the Si sites with a smaller number of next-nearest neighbor Al atoms. The mean value of the change in chemical shift per added Al on fourth nearest neighbor sites is ~2.8 ppm [2.3 ppm if Si(3Al) is excluded]. This value is similar to the results of recent QM/MM calculations and is somewhat larger than those previously reported for faujasite and LTA framework zeolite (~1.4 and 1.3 ppm). This difference correlates with the overall denser structure of analcime, including smaller cages and shorter Si-fourth neighbor distances. Combining these results with the known changes in $^{29}$Si chemical shifts for framework silicates due to changes in the first coordination shell, tetrahedral polymerization and second neighbor AI for Si substitution for tetrahedrally coordinated Si, we present an empirical relation between the changes in $^{29}$Si chemical shift and interatomic distance between Si and nearby atoms.

Keywords: Analcime, intermediate range structure, $^{29}$Si NMR, Si/Al ratio, fourth nearest neighbor

INTRODUCTION

Solid-state NMR is a powerful tool for studying local structural environments in silicate and aluminosilicate materials and can probe, for instance, the degree of polymerization, coordination number, structural and compositional environments up to several coordination shells, and the types of local structures present for atoms on crystallographically equivalent sites (e.g., Mägi et al. 1984; Engelhardt and Michel 1987; Kirkpatrick 1988; Sternberg and Priess 1993; Stebbins 1995; Lee and Stebbins 1999). $^{29}$Si NMR is widely used in the study of silicate materials, because it has a relatively large chemical shift range compared with other nuclei and is free from line broadening due to nuclear quadrupolar interactions. High-resolution $^{29}$Si MAS NMR techniques have been applied to many silicate mineral groups including zeolites, clays, feldspars, and silicas, as well as aluminosilicate glasses and melts (e.g., Weiss et al. 1987; Phillips et al. 1988, 1992; Xiao et al. 1993; Ward and McKague 1994; Myers et al. 1998; Stebbins 1995 and references therein; Lee and Stebbins 1999; Neuhoff et al. 2003; Nanba et al. 2004). These experimental studies have demonstrated correlations between $^{29}$Si NMR chemical shifts and empirical parameters describing the structural configurations around Si, including coordination number, Si,Al tetrahedral polymerization, Si-O bond length, and Si-O-Si bond angle, as well as more theoretical considerations such as bond hybridization and group electronegativity (Smith and Blackwell 1983; Engelhardt and Michel 1987; Kirkpatrick 1988; Sherriff and Gundy 1988; Sternberg and Priess 1993; Lee and Stebbins 1999; Liu et al. 2005). Quantum chemical calculations of $^{29}$Si NMR chemical shifts provide complementary insight into the origins of these correlations (Bussem et al. 1997; Valerio et al. 1999; Casanovas et al. 2000; Xue and Kanzaki 2000; Liu et al. 2005; Dedeček et al. 2009). Most of these empirical and theoretical correlations for silicate minerals explicitly take into consideration only parameters related to relatively short-range structure, and the effects of intermediate-range structure beyond the second nearest neighbors are less well documented.

Previous experimental and computational studies have shown, however, that such effects are likely to be measureable. Work on synthetic faujasite and LTA framework zeolites has shown that the $^{29}$Si chemical shifts for Si on tetrahedral sites with a given number of Al next-nearest neighbors [Si(nAl)] become more negative (more shielded) with increasing bulk Si/Al ratio (Klimowski et al. 1982; Newsam 1985). Newsam (1985) also reports changes in chemical shift per added fourth nearest neighbor [Si-O-(Si,Al)-O-(Si,Al)] atom. Most published quantum chemical calculations of $^{29}$Si chemical shifts for zeolites use clusters that extend to only the third nearest neighbor O atoms [Si-O-(Si,Al)-O] (Bussem et al. 1997; Valerio et al. 1999). Recent work by Dedeček et al. (2009) using density functional theory/