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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 Al 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