

Si-Al disorder and solid solutions in analcime, chabazite, and wairakite

PHILIP S. NEUHOFF,^{1,2,*} JONATHAN F. STEBBINS,² AND DENNIS K. BIRD²

¹Department of Geological Sciences, University of Florida, Gainesville, Florida 32611-2120, U.S.A.

²Department of Geological and Environmental Sciences, Stanford University,
Stanford, California 94305-2115, U.S.A.

ABSTRACT

Quantitative determination of the abundance of Si(*n*Al) tetrahedral structural units (where *n* = 0, 1, 2, 3, or 4) through analysis of ²⁹Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra was used to assess the state of Si-Al disorder in the zeolites analcime [(NaAl)_{*x*}Si_{48-*x*}O₉₆·16H₂O], chabazite [(Ca_{0.5},Na,K)_{*x*}Al_{*x*}Si_{12-*x*}O₂₄·12H₂O], and wairakite [CaAl₂Si₄O₁₂·2H₂O]. Short-range Si-Al ordering in chabazite and analcime is a regular function of Al mol fraction and is fully consistent with Al avoidance, as has generally been reported for zeolites not subjected to heat treatment. The results of this study and previously reported ²⁹Si MAS NMR spectra suggest that natural analcime samples are more Si-Al ordered than either their synthetic counterparts or chabazite. Cluster variation method (CVM) calculations were used to calculate the configurational entropy (*S*_{CON}) due to Si-Al disorder in chabazite and analcime. The calculations predict that long-range Si-Al ordering develops when Al occupies 5 out of 12 tetrahedral sites in chabazite and synthetic analcime and 17 out of every 48 tetrahedral sites in natural analcime. The difference between the calculated entropies and ideal entropies of mixing was used to derive activity-composition relationships for Si-Al substitution in these frameworks. Comparison between calculated values of *S*_{CON} and the results of calorimetric and phase equilibrium studies on analcime indicate that the CVM accurately assesses *S*_{CON}. The ²⁹Si MAS NMR spectrum obtained for natural wairakite indicates that this mineral is largely Si-Al ordered, but comparison with a previously published spectrum indicates that natural and synthetic wairakites can exhibit significant variation in Si-Al disorder.