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Na, K, Rb, and Cs exchange in heulandite single crystals: Diffusion kinetics

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ABSTRACT

Diffusion-exchange kinetics were determined at temperatures between 320 and 425 K for Na^+ in single crystals of natural heulandite, $Na_{0.96}Ca_{3.54}K_{0.09}(Al_{8.62}Si_{27.51}O_{72})\cdot nH_2O$, and K^+, Rb^+, and Cs^+ for Na^+ in Na-exchanged heulandite. Cation diffusion was measured on (010) cleavage plates with the aid of a polarizing microscope. This is possible because the optical properties, in particular the extinction angle, vary with the chemical composition of the channel occupants. This optical method is restricted to platy zeolites of monoclinic or triclinic symmetry where the channels are parallel to the crystal plate. Unlike conventional measurements, this method does not require the determination of the surface area of the zeolite.

No indication of anisotropic diffusion was observed on (010) plates for any of the exchanged cation pairs. Diffusion coefficients (D) show that the diffusion rate of $Na^+ \rightarrow Ca^{2+}$ is much slower than those of $K^+ \rightarrow Na^+$, $Rb^+ \rightarrow Na^+$, and $Cs^+ \rightarrow Na^+$, because of the strong Coulombic interaction of Ca^{2+} with the tetrahedral framework compared with an exchange of monovalent species. The activation energy (E_a) and the pre-exponential factor (D_0) were calculated from the variation of D with temperature for each diffusing cation. Comparable values of E_a for $K^+ \rightarrow Na^+$ and $Rb^+ \rightarrow Na^+$ suggest a similar diffusion process, while the lower value of E_a, combined with relatively low diffusion rates for $Cs^+ \rightarrow Na^+$ implies a different diffusion mechanism for Cs^+.