

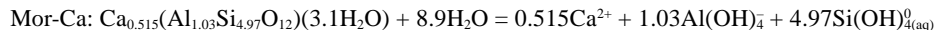
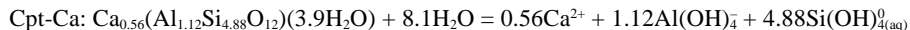
Solubility and stability of zeolites in aqueous solution: II. Calcic clinoptilolite and mordenite

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ABSTRACT

The solubilities of Ca-exchanged clinoptilolite (Cpt-Ca) and Ca-exchanged mordenite (Mor-Ca) have been measured in aqueous solutions between 25 and 275 °C and at saturated water vapor pressures. Natural zeolites were cation exchanged to close to Ca end-member composition (90% for Cpt-Ca, and 98% for Mor-Ca). The controlling dissolution reactions may be written as:



These reactions are reversible as shown by equilibrium constants calculated for approach from under- and supersaturation. The $\log K_{\text{sp}}$ for Cpt-Ca increases from -26.9 at 25 °C to a maximum of -16.9 at 275 °C, whereas for Mor-Ca the equilibrium constant varies from -25.3 at 25 °C to -17.7 at 265 °C. The solubilities for both zeolites increase with increasing temperature showing a positive enthalpy for the dissolution reaction. At lower temperatures Cpt-Ca is slightly more soluble than Mor-Ca, which agrees with natural observations where mordenite and clinoptilolite commonly occur together spatially but mordenite is in general the higher-temperature phase. A comparison with other exchanged clinoptilolites indicates that Cpt-Ca is more stable than the Na, K, and Mg varieties. The results demonstrate that the exchanged cation has a large effect on the solubility behavior, and that divalently exchanged varieties are less soluble than monovalent varieties. From the solubility constants, the standard Gibbs free energies of formation for hydrous Cpt-Ca and Mor-Ca at 25 °C and 1 bar were determined to be -6387 ± 5 kJ/mol and -6275 ± 7 kJ/mol respectively. However, compared to the hydration states and the aluminosilicate structure, the effect of the cation on the Gibbs free energies of formation is small.