

## **Nucleation and growth kinetics of analcime from precursor Na-clinoptilolite**

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### **ABSTRACT**

The kinetics and mechanism of analcime formation from precursor Na-clinoptilolite (Cpt-Na) and Na-mordenite (Mor-Na) were investigated from 125–225 °C, pressures up to 34.5 MPa, and pH = 9.2–10.7. By using batch and flow-through experimental methodologies, compositions of solids and solutions were monitored to track reaction progress, determine rates of analcime nucleation and growth, and evaluate the rate dependency of these processes on aqueous supersaturation. Analcime formation proceeds via a clinoptilolite (or mordenite) dissolution→analcime nucleation→analcime growth sequence. Synthetic analcime crystals are similar in morphology (trapezohedron to cubic trapezohedron) and composition (Si/Al = 2.1–2.7) to sedimentary analcimes formed during the low-grade alteration of crustal rocks, evidence that the experimental reaction mechanism is similar to that in natural environments.

Rates of analcime nucleation were approximated by evaluating the time-dependence of the size and number of particles and range between  $10^{9.80}$  and  $10^{11.88}$  per h per  $\text{cm}^3$  at 150° and 225 °C, respectively. The nucleation rate is a function of temperature and degree of supersaturation:  $\ln \text{rate} = 56.76 - 15978.9/T + 2.99 \times 10^{-4} \cdot \Delta G_r$ , where  $\Delta G_r$  is the free energy change of analcime precipitation and  $T$  is temperature in Kelvins. This rate equation is consistent with an apparent activation energy of analcime nucleation ( $E_{a,n}$ ) of  $132.8 \pm 8.3$  kJ/mol. Although conditions were thermodynamically favorable for analcime formation at 125 °C, nucleation was not detected after 144 hours. These data suggest that diagenetic timing of the clinoptilolite to analcime transformation is principally controlled by kinetics rather than by thermodynamic equilibrium.

Rates of analcime growth were estimated by measuring particle size distributions. Average growth rates ranged from 0.15  $\mu\text{m}/\text{h}$  at 150 °C to 0.396  $\mu\text{m}/\text{h}$  at 225 °C, and are consistent with an apparent activation energy of analcime growth ( $E_{a,g}$ ) of  $77.1 \pm 9.4$  kJ/mol. These nucleation and growth parameters are combined to successfully model the evolution of analcime particle size distributions. The experimental methods developed in this study demonstrate the use of hydrothermal flow-through methods in the study of zeolite transformations.