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STRUCTURAL CHANGES IN ANALCITES AND Na–P ZEOLITES CAUSED BY CATION EXCHANGE AT ROOM TEMPERATURE AND DEHYDRATION UNDER CONTROLLED pH_2O

by

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ABSTRACT

ALTHOUGH zeolites are usually thought of as substances that undergo continuous water loss without structural change, there have been very few experiments to establish this fact.

The present report covers an extensive experimental study of the Na–P (phillipsite–harmotome) and analcite families. The influence of cation exchange (even at room temperature) of K, Ca, Ba, Ni, Co, etc., is shown to cause substantial changes in the powder X-ray pattern, reflecting changes of symmetry as well as unit cell parameters.

Using controlled partial pressures of H_2O in the range of about 10^{-3} to 10^{0} atm and recording thermogravimetric balances, the compositional changes with temperature have been recorded, and the kinetics of each step-wise change also studied. High-temperature X-ray diffraction, under the same pH_2O conditions, provides an indication of the structural changes corresponding to the compositional breaks. Dehydration studies of the Na–P forms show the most remarkable complexity with as many as five different structures existing below 400°C. The K^{ex} form appears to be the least complex. Discontinuities appear in weight-loss curves of both the parent and Sr-exchanged form of the normal analcite and in the Ca-exchanged form of the silica-rich analcite. The latter undergoes a reversible 20% loss in water content at 425°C (7.9 mm Hg pH_2O) corresponding to a reversible 3% contraction of its cell edge. The transformation exhibits a 50° hysteresis on cooling. The effect of cation content on water retentivity is profound. K-containing samples begin to lose a substantial amount of water some 50–100°C lower than the corresponding Na samples, although both become fully dehydrated at about 400°C. Ca- and Li-containing samples dehydrate much more slowly with increasing temperature. Wairakite approaches complete dehydration only at 600°C. The overall dehydration behavior accords closely with the relative heats of hydration of the respective ions.

General conclusions that can be drawn from the results are:

1. Many zeolites, depending equally on the parent structure and exchangeable cation, undergo several steps in the dehydration process.
2. Structural changes correspond to first-order dehydration reactions, continuous or second-order dehydration reactions over a temperature range, and true polymorphic changes.

Finally, the results of hydrothermal experiments are used to indicate the enormous differences between the stable and several metastable dehydration reaction series. In both the Na–P and analcite families, true crystalline mixing and unmixing occurs between Na^{ex} and K^{ex}, and Na^{ex} and Ca^{ex} members in the range below 100°C.

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