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LETTER

A $P_{\text{H}_2\text{O}}$ -dependent structural phase transition in the zeolite natrolite

HSIU-WEN WANG* AND DAVID L. BISH

Department of Geological Sciences, Indiana University, 1001 East 10th Street, Bloomington, Indiana 47405, U.S.A.

ABSTRACT

The crystal structures of natrolite and its dehydrated high-temperature phases (α 1- and α 2-metanatrolite) have been determined from powder X-ray diffraction measurements as a function of temperature and partial pressure of water ($P_{\text{H}_2\text{O}}$) to characterize the phase transition behavior. The evolution of crystal structure as a function of temperature shows two different phase transitions, depending on the $P_{\text{H}_2\text{O}}$, with α 1-metanatrolite occurring at elevated $P_{\text{H}_2\text{O}}$ and α 2-metanatrolite occurring at low $P_{\text{H}_2\text{O}}$. Our discovery of α 2-metanatrolite implies the existence of more than one transition mechanism, which we correlate with the migration of Na^+ ions and the *rate* of evolution of H_2O molecules. The transition behavior is rationalized in terms of two cooperating mechanisms: (1) dehydration-induced processes, which determine the phase transition temperature; and (2) thermally induced processes, which determine how the framework and its extraframework cations are modified.

Keywords: Phase transition, natrolite, crystal structure, Rietveld refinement, TGA