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Hydrogen-bonded water in laumontite I: X-ray powder diffraction study of water site occupancy and structural changes in laumontite during room-temperature isothermal hydration/dehydration

THRÁINN FRIDRIKSSON,[1,*] DAVID L. BISH,[2] AND DENNIS K. BIRD[1]

[1]Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.
[2]Hydrology, Geochemistry, and Geology, MS D469, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.

ABSTRACT

The response of the laumontite crystal structure to hydration/dehydration was evaluated using Rietveld refinements with XRD data collected under controlled P_{H_2O} conditions at ~28.5 °C. Refined water contents per unit cell (unit-cell formula: $Ca_4Al_8Si_{16}O_{48}\cdot nH_2O$) ranged between 12.5 H_2O at 0.11 mbar P_{H_2O} and 17.3 H_2O at 37.6 mbar. The occupancy of the two water sites hosting hydrogen-bonded water molecules, W5 and W1, ranged from 13% to 100% and from 2% to 86%, respectively. During hydration of W5, between 0.11 and 5 mbar, the unit cell expanded continuously and reversibly from 1327 to 1348 Å^3. The unit-cell volume remained nearly constant between 5 and 28 mbar. The hydration/dehydration of W1 exhibited hysteresis; hydration occurred at ~29 mbar and dehydration at ~24 mbar. During hydration of W1 at ~29 mbar the unit cell expanded from 1351 to 1384 Å^3. Further hydration of W1 above 29 mbar resulted in gradual and reversible unit-cell expansion to 1386 Å^3 at 37.6 mbar. Hydration/dehydration of W5 is a continuous reaction typical for zeolites. In contrast, the hydration/dehydration of W1 at room temperature is discontinuous, as manifested by the presence of two laumontite phases during hydration and dehydration. Unit-cell parameters of the two coexisting laumontite phases observed under these conditions are consistent with a vacant W1 site and ~80%-occupied W1 site, respectively. Gradual unit-cell expansion above 29 mbar due to increased P_{H_2O} and increased occupancy of W1 indicate that hydration of the remaining 20% of the W1 site proceeds continuously.