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Hydrogen-bonded water in laumontite II: Experimental determination of site-specific thermodynamic properties of hydration of the W1 and W5 sites

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ABSTRACT

Isothermal vapor sorption experiments under controlled partial pressures of H_2O (between 0.1 and 30 mbar, at 23.4, 30.1, 49.5, 64.5, and 79.3 °C) and liquid water immersion calorimetry experiments at 25.0 °C were conducted to determine standard molar thermodynamic properties of hydration of the W1 and W5 sites in laumontite that host hydrogen-bonded water. A Langmuir adsorption model was used in a thermodynamic analysis of the isothermal adsorption data for the W5 site together with a symmetrical regular solution model. Resulting values for the standard molar Gibbs energy and entropy of hydration of the W5 site relative to liquid water are –8430 ± 113 J/mol and –16.7 ± 2.1 J/(mol·K), respectively, and the Margules parameter, W_G, is 1590 ± 63 J/mol. The standard enthalpy of hydration of the W1 site was determined by liquid-water immersion calorimetry experiments on laumontite containing vacant W1 and fully occupied W5, W2, and W8 sites. Discontinuous hydration and dehydration of W1 at 23.4 ± 0.7 °C and 24 ± 1 mbar P_{H_2O} was used to constrain the molar Gibbs energy of hydration of this site. Resulting values for standard molar Gibbs energy of hydration and enthalpy of W1 relative to liquid water are –380 ± 170 and –8800 ± 1150 J/mol, respectively. Isothermal adsorption at 23.4 °C and isobaric thermogravimetric experiments indicate that during dehydration of W1, only 0.83 moles of water are released from the crystal structure and 0.17 moles are relocated to a disordered site that has energetic properties similar to the W8 site. Calculations using the thermodynamic data determined in this study indicate that the water content of laumontite in equilibrium with liquid water ranges from ~4.5 H_2O per 12 framework O atoms at room temperature and one bar pressure to ~3.5 H_2O at 250 °C and at liquid-vapor saturation pressure for water.