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Title: Water-bearing minerals on Mars: Source of observed mid-latitude water?

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Introduction: The Odyssey spacecraft documented the existence of heterogeneously distributed hydrogen at martian mid-latitudes, suggesting that large areas of the near-equatorial highlands contain near-surface deposits of “chemically and/or physically bound H₂O and/or OH” in amounts up to 3.8% equivalent H₂O [1]. Shallow occurrences of water ice are not stable near the martian equator [2, 3], making the hydrogen deposits at these latitudes somewhat enigmatic. Clay minerals and zeolites have both been proposed as possible water-bearing constituents on Mars, and both are common terrestrial alteration products of hydrovolcanic basaltic ashes and palagonitic material comparable to those that may be widespread on Mars [e.g., 4]. Smectites within martian meteorites, attributed to hydrous alteration on Mars rather than on Earth [5], provide direct evidence of clay minerals from Mars. In addition, new thermal emission spectrometer (TES) data provide good evidence for unspecified zeolites in martian surface dust [6]. The nature of the hydrogen-containing material observed in the equatorial martian regolith is of particular importance to the question of whether hydrous minerals have formed in the past on Mars. Also, whether these minerals exist in a hydrated (i.e., containing H₂O molecules in their structures) or dehydrated state is a crucial question. The existence of hydrous minerals is also important in connection with their possible role in affecting the diurnal variation of the martian atmosphere, in their potential role in unraveling the paleohydrology and paleobiology of Mars, and in their possible use as a water resource to support exploration of the martian mid-latitudes.

Little, if any, data are available allowing prediction of the hydration state of these minerals under the low-T and low-P(H₂O) conditions existing on the surface of Mars. As chabazite is a common alteration product in the types of rocks presumed to occur on Mars, we have used a combination of thermogravimetric methods to quantify the hydration energetics of chabazite and determine whether this representative zeolite would contain H₂O under martian mid-latitude near-surface conditions. The structure of chabazite (Ca₂Al₄Si₈O₂₄·12H₂O) is made up of four- and eight-membered rings, giving a structure with large elliptical extraframework sites that can contain both exchangeable cations and H₂O molecules.

Methods and Results: Data were measured for chabazite samples from Christmas, Arizona, and Wassons Bluff, Nova Scotia. Isothermal and dynamic ther-

mo gravimetric analysis (TGA) data were measured using a DuPont 951 TGA with automated relative humidity (RH) control.

Dynamic TGA data, measured at 2 to 10°C/min heating rates with an N₂ purge, show the existence of two distinct types of H₂O molecules, one lost from 23 to ~187°C and a second lost from ~187 to 300°C (Figure 1). These TGA data were modeled assuming equilibrium dehydration occurring at an H₂O-vapor pressure of 0.03 bar (i.e., 100% RH at room temperature, as supported by other experiments in our laboratory). Values for the Gibbs free energy of hydration, enthalpy of hydration, and non-ideal mixing parameters were regressed from the TGA data using equation 12 of [7], assuming $\Delta\bar{C}_{p,Hy} = R$ (8.314 J/mol-K) and $V_{H_2O}^{Zeo} = 0$. Because the TGA data demonstrate the existence of two distinct dehydration reactions, two independent regressions were performed and the two simulated TGA curves were then added to give the simulated curve in Fig. 1. These regressions provided values for the partial molar free energy and enthalpy of hydration of -17.1 and -49.5 kJ/mol, respectively, for the low-T reaction and -35.96 and -68.9 kJ/mol, respectively, for the high-T reaction (simulations also included two temperature-independent coefficients).

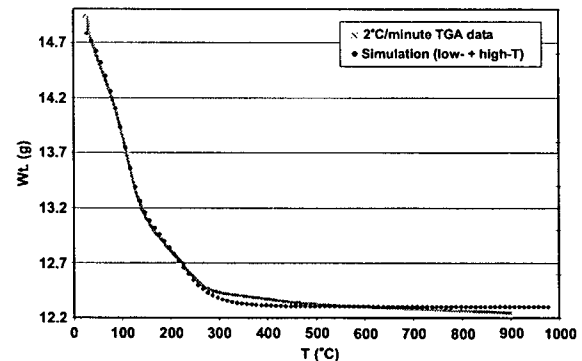


Figure 1. Measured and simulated TGA curves for chabazite, showing two distinct weight-loss events.

Isothermal TGA data were measured as a function of RH from 0% to 95% and back to 0% RH at 25, 35, 50, 70, 100, 150, and 200°C. These data provided a family of $\ln K$ vs. θ curves (θ = fractional water content, $K = \theta/[(1-\theta)P]$, where P is the H₂O vapor pressure in bars). These curves also suggested the existence of two distinct hydration/dehydration events; one <100°C and another >100°C. Initial attempts to fit all isotherms

using the methods of [8] provided poor fits and unrealistic thermodynamic data. We then separately fit the 25, 35, 50, and 70°C isotherms together and the 150 and 200°C data together, resulting in excellent fits (r^2 values of 0.978 and 0.998 for the low- and high-temperature data, respectively). These fits gave values for the partial molar free energy and enthalpy of hydration of -24.1 and -66.2 kJ/mol, respectively, for the low-T reaction and -67.1 and -104.9 kJ/mol, respectively, for the high-T reaction (fits included two temperature-independent coefficients). These partial molar quantities are significantly different from the values derived from dynamic TGA data, but integral quantities are closer. Providing added confidence in the fits, the regressed high-T thermodynamic values provide a good fit to the low- θ portion of the 100-°C data (Figure 2), and similarly for the low-T values and the high- θ portion. Figure 2 shows that a model assuming a single hydration/dehydration reaction does not provide an adequate fit to all of the data.

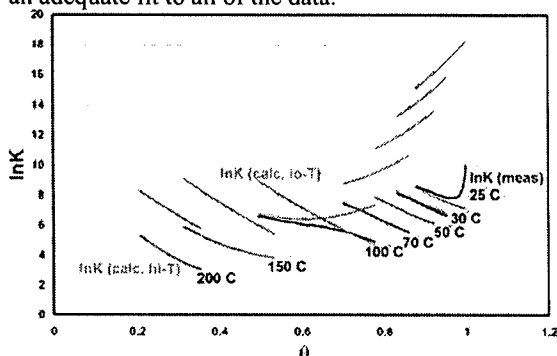


Figure 2. $\ln K$ vs. θ for isothermal TGA data (data-blue; low-T fits-magenta; high-T fits-green). Note that the 150 and 200°C fits are difficult to see because they almost perfectly overlap the data.

Thermodynamic values obtained from isothermal and dynamic TGA can be used to calculate the degree of hydration of chabazite as a function of T or of $P(\text{H}_2\text{O})$. Simulations using the values from isothermal TGA data suggest that chabazite would retain the majority of its high-T H_2O even at equator daytime temperatures (Figure 3). The high-T H_2O in chabazite is held quite strongly, and we can state with confidence that if chabazite formed in the past on Mars, its present-day equilibrium state would be at least partially hydrated. The low-T H_2O is held much less strongly, and these H_2O sites would range from full to empty during a night-day temperature excursion (160-280K). Simulations using the thermodynamic values from the dynamic TGA data show similar trends, although the details of the simulated curves are different. The θ values calculated using dynamic TGA data decrease

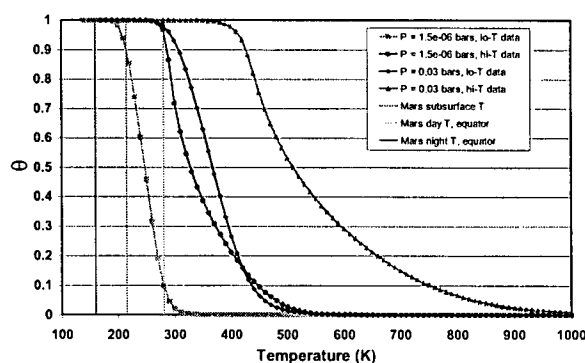


Figure 3. Fractional H_2O content of chabazite, calculated for pressures of 0.03 (100% RH) and 1.5×10^{-6} bars, using low- and high-T thermodynamic values from isothermal TGA data.

more abruptly as a function of temperature than do the θ values shown in Figure 3, probably a result of the absence of isothermal data above 200°C. Values from dynamic TGA confirm that the high-T H_2O sites would be fully occupied under plausible martian surface conditions. Likewise, thermodynamic values for the low-T H_2O from dynamic experiments suggest that these H_2O sites would vary from full to vacant over the temperature range shown in Figure 3.

Both dynamic and isothermal TGA data for chabazite support the presence of two distinct types of H_2O molecules, requiring that the thermal data be analyzed assuming two hydration/dehydration reactions. These quantitative thermodynamic data on H_2O in chabazite demonstrate that the equilibrium hydration state under martian surface conditions is such that the high-T H_2O site is essentially full. The energetics of the low-T H_2O site are such that this site may hydrate and dehydrate on a daily scale. These data also demonstrate that hydrated minerals such as chabazite could account for the observed mid-latitude water on Mars.

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