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Heat capacity of hydration in zeolites

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ABSTRACT

Dehydration of zeolites is a critical factor in their stability, effectiveness as storage media for thermal energy, and influence on the thermal evolution of radioactive waste repositories. Prediction of the hydration states of zeolites as a function of temperature, pressure, and water activity is often hampered by limited data on the heat capacity changes associated with (de)hydration reactions. This property is often assumed to be temperature invariant based on statistical-mechanical reasoning. To test this assumption, heat capacities of homologous hydrated and dehydrated zeolites (analcime, natrolite, wairakite) were measured by differential scanning calorimetry from 130 to 600 K that were subsequently used to calculate the heat capacity of hydration. Simultaneous monitoring of sample mass was used to discard data for hydrated phases affected by thermal effects associated with dehydration at elevated temperature. All three phases exhibited marked variations in the heat capacity of hydration with temperature. This behavior appears to be related to second-order phase transitions involving the water molecules. In wairakite, a second-order phase transition associated with a change in framework symmetry from monoclinic to tetragonal only occurs in the hydrated form, and leads to a prominent peak in the temperature dependence of the heat capacity of hydration. Above the transition temperature, the heat capacity of hydration becomes negligible. Neglecting the temperature dependence of the heat capacity of hydration in zeolites can have a significant effect on thermodynamic properties of dehydration reactions regressed from equilibrium observations at elevated temperatures.

Keywords: Zeolite, analcime, wairakite, natrolite, heat capacity, differential scanning calorimetry, hydration, phase transitions

INTRODUCTION

The thermal behavior of zeolites is an important consideration for evaluating the consequences of temperature changes in geologic, experimental, and engineered systems. Progressive, often reversible, dehydration accompanying heating of zeolites is well established (e.g., van Reeuwijk 1974; Bish and Carey 2001). Changes in water content of zeolites as a function of temperature and pressure can have a profound effect on predictions of their stability in geologic environments (e.g., Helgeson et al. 1978; Carey and Bish 1996; Neuhoff and Bird 2001; Chipera and Apps 2001). The enthalpic consequences of dehydration and rehydration in these materials is an important consideration in modeling the thermal evolution of radioactive waste repositories (e.g., Smyth 1982; Carey and Bish 1996; Bish et al. 2003; Long and Ewing 2004) and are widely employed in heat-pump technologies (e.g., Boddenberg et al. 2002; Kasai et al. 1994; Petrova et al. 2001; Tchernev 2001).

The importance of hydration and dehydration reactions in zeolites has led to considerable experimental study of the energetics of this process. This is typically accomplished through equilibrium observations (e.g., Carey and Bish 1996; Wilkin and Barnes 1999; Fridriksson et al. 2003; Fialips et al. 2005; Jänchen et al. 2006) and calorimetric measurements (e.g., Barrer and Cram 1971; Johnson et al. 1982, 1991, 1992; Guliev et al. 1989; Valueva and Goryainov 1992; Carey 1993; Mizota et al. 1995; Kiseleva et al. 1996a, 1996b, 1997, 2001; Ogorodova et al. 1996, 2002; Carey and Bish 1997; Muller et al. 1998; Drebushchak 1999; Shim et al. 1999; Yang and Navrotsky 2000; Yang et al. 2001; Petrova et al. 2001). Thermodynamic properties for reactions of the form

$$Z + nH_2O_{(g)} \leftrightarrow Z{\cdot}nH_2O \tag{1}$$

where Z and $Z{\cdot}nH_2O$ represent the dehydrated and hydrated homologs, respectively, derived from equilibrium observations often differ considerably from those determined calorimetrically (e.g., Bish and Carey 2001). In addition, the results of different calorimetric methods are inconsistent with each other (Barrer and Cram 1971; Yang et al. 2001; Bish and Carey 2001). Many potential causes for these discrepancies have been cited, including differing sample compositions, different reference states, lack of attainment of equilibrium, and irreversible changes to samples during dehydration (Bish and Carey 2001; Fialips et al. 2005). One of the complications encountered in retrieving thermodynamic data from equilibrium observations is that typically the heat-capacity change across reaction 1 [$\Delta C_{P(r)}$] needs to be known independently to minimize the number of variables in the regression scheme (e.g., Carey and Bish 1996; Fridriksson et al. 2003; Fialips et al. 2005). As discussed below, direct determinations of $\Delta C_{P(r)}$ are difficult, particularly at elevated temperature. The numeric consequences of $\Delta C_{P(r)}$ are most pronounced at elevated temperatures as this function is integrated over temperature to derive the enthalpy, entropy, and Gibbs energies of reaction

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[$\Delta H_{(r)}$, $\Delta S_{(r)}$, and $\Delta G_{(r)}$, respectively]. Thus, the assumptions concerning the magnitude of $\Delta C_{P(r)}$ can have an important effect on the magnitudes of other thermodynamic properties regressed from phase-equilibrium observations, particularly those made at elevated temperatures. This effect may represent another source of the discrepancy between thermodynamic properties retrieved from phase-equilibria and calorimetric experiments.

Determination of $\Delta C_{P(r)}$ is complicated by dehydration of zeolites at elevated temperature. Previous measurements of $\Delta C_{P(r)}$ for zeolite (de)hydration reactions have involved direct determination of C_P for homologous hydrated and dehydrated zeolites through adiabatic, drop, or differential scanning calorimetric methods (e.g., Basler and Lechert 1972; Johnson et al. 1982, 1991, 1992; Vučelić and Vučelić 1985). Measurement of C_P for hydrated zeolites at elevated temperatures is often frustrated by excess heat effects due to dehydration of the sample (Carey 1993). This typically limits the range of temperatures over which C_P for hydrated zeolites and $\Delta C_{P(r)}$ for dehydration reactions can be determined, although some workers have attempted to correct drop calorimetric results on hydrated zeolites for the heat of hydration to extend the temperature range over which these properties can be determined (e.g., Johnson et al. 1983, 1985, 1991, 1992). More commonly, $\Delta C_{P(r)}$ is assumed to be independent of temperature (e.g., Carey and Bish 1996; Fridriksson et al. 2003; Fialips et al. 2005).

EXPERIMENTAL METHODS

Materials and sample preparation

Experiments were conducted on phase-pure samples of the natural zeolites analcime, natrolite, and wairakite. The natrolite sample (NAT001 from Neuhoff et al. 2002) occurs as masses of white crystals filling veins in a metabasaltic tectonic inclusion at the Dallas Gem Mine, San Benito Co., California. The analcime sample (ANA002 from Neuhoff et al. 2003) is from a zeolite-facies metabasalt outcrop at Maniilat on the island of Qeqertarsuaq in West Greenland and prepared from a 1.5 cm euhedral crystal of opaque analcime. Wairakite (sample ANA004 from Neuhoff et al. 2003) was obtained from J.-G. Liou from stock remaining from his previous phase-equilibrium experiments (Liou 1970, 1971) and originated from the Onikobe geothermal system (see Seki et al. 1969 for details about this sample).

Pure mineral separates were hand-picked from slightly crushed megascopic mineral samples and then ground in an agate mortar. Sample purity was confirmed by powder X-ray diffraction (XRD) and ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. Sample compositions for analcime, chabazite, and wairakite were previously determined by electron-probe microanalysis (EPMA) at Stanford University on an automated JEOL 733A electron microprobe (see Neuhoff et al. 2002, 2003, for analytical details). The composition of analcime determined by EPMA was slightly more Si-rich than that consistent with the ^{29}Si MAS NMR results, and the latter results were assumed more representative of the composition (see Neuhoff et al. 2004 for a detailed discussion of this issue). Water contents were determined by measuring mass loss between 298 and 1000 K by scanning-heating TGA at a heating rate of 15 K/min on the instrument described below. Sample compositions and molecular masses consistent with these analyses were: analcime ($Na_{0.97}Al_{0.97}Si_{2.03}O_6 \cdot 1.015H_2O$; mass 219.7676 g/mol), dehydrated analcime ($Na_{0.97}Al_{0.97}Si_{2.03}O_6$; mass 201.4821 g/mol), natrolite ($Na_2Al_2Si_3O_{10} \cdot 2H_2O$; mass 380.224 g/mol), dehydrated natrolite ($Na_2Al_2Si_3O_{10}$; mass 344.193 g/mol), wairakite ($Ca_{0.94}Na_{0.08}Al_{1.96}Si_{4.04}O_{12} \cdot 1.96H_2O$; mass 433.164 g/mol), and dehydrated wairakite ($Ca_{0.94}Na_{0.08}Al_{1.96}Si_{4.04}O_{12}$; mass 397.835 g/mol). To extend the range of temperatures over which C_P could be determined for analcime, a partially hydrated sample (composition $Na_2Al_2Si_3O_{10} \cdot 0.285H_2O$; mass 206.6165 g/mol) was prepared by incomplete thermal dehydration.

Calorimetry

Heat capacities were measured in the temperature range 140 to 725 K by scanning DSC measurements on a Netzsch STA 449C Jupiter simultaneous DSC-TGA apparatus. The temperature range was split into two overlapping regions to optimize the heat transport characteristics of the carrier gas: cryogenic experiments (140 to 350 K) were conducted under flow of ultrapure He, whereas ultrapure N_2 was used for experiments at higher temperatures (typically 225 to 725 K). Experiments on analcime homologs were only performed over the higher temperature range. Gas flow was maintained at ~30 mL/min using mass-flow controllers. A multipoint temperature calibration curve was developed using the melting points of H_2O, Ga, In, Sn, Bi, Zn, and Al along with the solid-solid transition points of ammonium dihydrogen phosphate, ammonium sulfate, cesium chloride and quartz (Cammenga et al. 1993; Gmelin and Sarge 2000; Höhne et al. 1990; Sabbah et al. 1999; Price 1995). Due to the incompatibility of these materials with the Pt-Rh crucible used in the experiments, temperature calibration was conducted in identical crucibles lined with a sub-mm thick insert of alumina. Caloric calibration was accomplished using the DSC response of synthetic sapphire (Gmelin and Sarge 2000; Sabbah et al. 1999; Sarge et al. 1994; Stølen et al. 1996). All experiments were conducted in Pt-Rh crucibles with unsealed, perforated lids using sample masses between 20 and 30 mg. Samples were run in triplicate with each experiment consisting of five separate runs: (1) a background correction with an empty crucible; (2) a single-crystal sapphire caloric standard; (3) the hydrated sample; (4) the dehydrated sample; and (5) repeat of the background correction. Standard response was compared between experiments to test for reproducibility. Companion experiments on quartz yielded C_P measurements within 1% of previously reported values.

RESULTS

Measured C_P for hydrated and dehydrated homologs of analcime, natrolite, and wairakite and partially dehydrated analcime are listed in Tables 1–3 and plotted as a function of temperature in Figures 1–3. In general, there was good agreement (<1% discrepancy) between C_P values determined under He and N_2 gases, and the results shown in Figures 1–3 are the average of these data. Data shown for hydrated homologs are reported only for conditions in which the simultaneous TGA signal did not indicate mass loss.

Hydrated wairakite exhibits a pronounced (lambda-type?) phase transition with a peak in C_P at ~424 K. Below that peak, C_P rises continuously without inflection from the low-temperature results. At temperatures above the peak, C_P decreases markedly by ~10% before the onset of dehydration. This transition is completely reversible provided that the experiment is stopped prior to dehydration; rehydration of wairakite is too slow for the hydrated form to be prepared from the dehydrated form (although slow rehydration occurred in samples that were exposed to humid air at ambient temperature for 18 months). This transition is completely absent in the dehydrated form as shown in Figure 1.

Another apparent lambda-type phase transition was observed in dehydrated natrolite with a peak in around 525 K. Figure 2b shows this transition in more detail. The lambda form begins around 460 K and the transition is complete at about 550 K. This transition is completely reversible. Close inspection of the TGA signal during this transition reveals a small mass change (~0.3% of total sample mass). It appears that this mass change is associated with desorption of N_2 gas from the sample, as the sample chamber was completely dry (having been flushed with ultrapure, dry N_2 for several hours above the dehydration temperature of natrolite and then evacuated three times to 10^{-4} Torr vacuum) and no water vapor was detected by an inline, flow-through humidity meter attached to the furnace exhaust. The heat effect associated with this reaction (taken to be the area between the C_P curve and the fit in Fig. 2b) is ~1.6 kJ per mole of dehydrated natrolite), which corresponds to a heat of desorption of ~37 kJ per mole of N_2). This latter value is similar in magnitude to that observed for N_2 absorption in other zeolites

TABLE 1. Heat capacities of hydrated and dehydrated natrolite and hydrated and dehydrated wairakite determined by DSC (in He)

T (K)	hydrated natrolite C_P, J/(mol·K)	dehydrated natrolite C_P, J/(mol·K)	hydrated wairakite C_P, J/(mol·K)	dehydrated wairakite C_P, J/(mol·K)
143.15	195.6	158.0	223.0	163.3
148.15	208.7	168.7	229.5	173.2
153.15	218.1	176.5	237.8	180.5
158.15	226.6	183.1	243.4	187.3
163.15	234.7	189.8	250.6	193.4
168.15	241.0	195.2	258.3	199.5
173.15	246.4	199.8	267.1	205.3
178.15	252.2	204.6	273.7	210.1
183.15	258.3	208.3	279.7	214.7
188.15	264.4	213.0	282.9	219.8
193.15	270.3	218.2	290.3	224.7
198.15	275.6	222.9	297.4	229.6
203.15	280.5	226.9	301.7	234.5
208.15	287.1	232.5	309.5	240.1
213.15	293.3	237.6	314.6	245.7
218.15	298.2	242.4	321.3	250.3
223.15	302.4	246.6	326.2	254.4
228.15	307.0	249.3	332.7	258.3
233.15	310.3	249.9	336.1	261.4
238.15	315.5	255.2	340.5	265.5
243.15	318.8	257.6	346.9	269.9
248.15	321.6	258.8	352.9	273.0
253.15	324.3	259.5	358.1	276.8
258.15	327.2		362.5	280.5
263.15	331.2		366.7	285.6
268.15	336.6		373.3	290.9
273.15	345.9		384.8	298.7
278.15			388.7	302.1
283.15			395.6	304.6
288.15			400.9	307.5
293.15			404.2	310.5
298.15			404.8	313.8

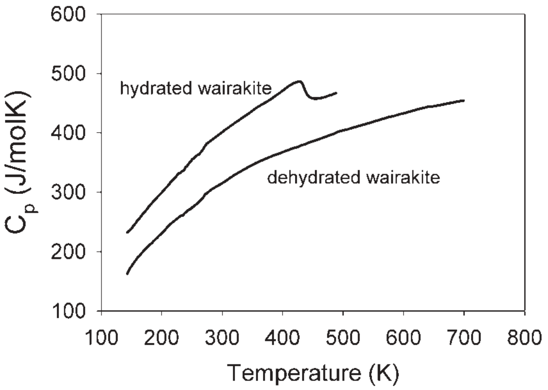

FIGURE 1. Heat capacity of hydrated and dehydrated wairakite determined in this study.

TABLE 2. Heat capacities of hydrated natrolite, wairakite, and analcime and partially hydrated analcime determined by DSC (in N_2)

T (K)	hydrated natrolite C_P, J/(mol·K)	hydrated wairakite C_P, J/(mol·K)	hydrated analcime C_P, J/(mol·K)	partially hydrated analcime C_P, J/(mol·K)
248.15				
253.15			203.6	
258.15			200.5	
263.15	332.3		200.7	
268.15	336.5		202.0	
273.15	340.3	380.8	203.4	
278.15	344.6	385.6	204.7	
283.15	348.8	389.5	206.2	
288.15	352.6	393.2	207.5	
293.15	356.6	397.0	208.7	
298.15	360.4	400.9	210.1	
303.15	364.5	404.9	211.5	
313.15	373.4	412.3	214.6	
323.15	382.0	419.4	217.4	
333.15	390.9	426.5	220.4	
343.15	398.8	433.3	223.7	
353.15	405.9	440.9	226.7	191.3
363.15	411.8	447.6	229.6	193.0
373.15	417.1	453.4	232.3	194.9
383.15	421.8	460.1	235.6	197.2
393.15	426.3	467.3		199.4
403.15	431.1	475.0		201.9
413.15		482.2		204.5
423.15		486.9		207.1
433.15		482.9		209.7
443.15		462.6		212.2
453.15		458.7		214.5
463.15		459.9		216.5
473.15		462.8		218.7
483.15		466.4		221.0
493.15				223.9

(e.g., Sebastian et al. 2005). Given the small mass of N_2 that is desorbed during this event, C_P for dehydrated natrolite was not adjusted for mass changes across this transition.

The onset of dehydration in analcime at ~375 K significantly limited the temperature range over which C_P for this phase, and $\Delta C_{P(r)}$ for reaction 1, could be evaluated. Consequently, C_P was also measured on a partially dehydrated analcime (with a water content corresponding to 28% hydration). This sample retained its water through ~500 K. The results are shown in Table 2 and Figure 3, where it can be seen that the temperature dependence of C_P for the partially dehydrated composition parallels those of the fully hydrated and dehydrated homologs. Assuming that there is no excess heat capacity across the hydrated analcime-dehydrated analcime solid solution (which seems likely given the lack of excess enthalpy across this solution; Ogorodova et al. 1996), then C_P for the partially hydrated form should obey the relation

$$C_{P[(\mathrm{NaAl})_{0.97}\mathrm{Si}_{2.03}\mathrm{O}_6\cdot 0.285\mathrm{H_2O}]} = C_{P[(\mathrm{NaAl})_{0.97}\mathrm{Si}_{2.03}\mathrm{O}_6]} + 0.285/1.015 \times \{C_{P[(\mathrm{NaAl})_{0.97}\mathrm{Si}_{2.03}\mathrm{O}_6\cdot 1.015\mathrm{H_2O}]} - C_{P[(\mathrm{NaAl})_{0.97}\mathrm{Si}_{2.03}\mathrm{O}_6]}\}. \qquad (2)$$

Over the range of temperature where data were collected for all three samples, this relationship holds within the estimated 1% uncertainty in the C_P measurements. Equation 3 was rearranged to estimate C_P for fully hydrated analcime from that of the partially dehydrated form (Fig. 4). It can be seen that there is generally good agreement between the estimated and measured values in the region of overlap. The combined data set in Figure 4 were used in the regressions presented below.

Smoothed functions of C_P as a function of T above 298.15 K were determined by fitting the data in Tables 1–3 and Figures 1–4 to the Maier and Kelley (1932) polynomial function

$$C_P = a + bT + cT^{-2} \qquad (3)$$

where a, b, and c are empirical fitting coefficients and T is the temperature in K. Results of these fits are shown in Table 4. The Maier and Kelley coefficients listed in Table 4 for wairakite describe the temperature dependence of C_P to the peak of the lambda-form; the onset of dehydration at temperatures just above this transition preclude evaluation of the temperature dependence of C_P at higher temperatures. The Maier and Kelly coefficients for dehydrated natrolite were regressed from the data in Figure

TABLE 3. Heat capacities of dehydrated natrolite, wairakite, and analcime determined by DSC (in N_2)

T (K)	dehydrated natrolite C_P, J/(mol·K)	dehydrated wairakite C_P, J/(mol·K)	dehydrated analcime C_P, J/(mol·K)
248.15	260.5		
253.15	262.3		
258.15	264.3		151.7
263.15	266.6		152.3
268.15	269.7		153.8
273.15	272.4	297.5	155.2
278.15	275.3	301.6	156.6
283.15	278.2	305.4	158.0
288.15	280.7	308.5	159.6
293.15	283.1	311.4	160.9
298.15	285.3	314.4	162.3
303.15	287.5	317.5	163.7
308.15	290.0	321.0	165.4
313.15	292.4	324.5	166.7
318.15	294.7	327.9	167.9
323.15	296.3	331.2	169.4
333.15	300.5	337.0	171.9
343.15	304.6	342.6	174.5
353.15	309.1	348.2	176.7
363.15	313.4	353.2	179.4
373.15	317.7	357.5	181.6
393.15	325.7	365.2	186.2
413.15	333.4	373.0	191.1
433.15	341.3	379.8	195.2
453.15	349.1	387.7	199.1
473.15	359.3	395.5	202.9
493.15	374.3	402.5	207.4
513.15	392.7	408.2	210.6
533.15	384.7	413.9	214.0
553.15	377.0	420.0	218.6
573.15	380.6	426.2	222.2
593.15	385.4	431.4	225.3
613.15	390.2	437.0	228.0
633.15	395.6	442.4	230.0
653.15		445.7	
673.15		449.8	
693.15		453.7	

2a outside of the lambda transition and led to a smooth representation of C_P over the whole range of temperature (Fig. 2b). In all cases, the polynomial of Equation 3 gave a satisfactory fit ($R^2 > 0.99$).

DISCUSSION

Comparison with previous results

The C_P data generated in this study for hydrated and dehydrated homologs of analcime and natrolite are compared to those obtained in previous studies in Figures 2 and 3. The data of Drebushchak (1990) were measured by DSC as was done in this study. The data generated by King (1955), King and Weller (1961), and Johnson et al. (1982, 1983) at temperatures below 350 K were measured by adiabatic calorimetry. The high-temperature (>350 K) C_P values obtained by Pankratz (1968) and Johnson et al. (1982, 1983) were regressed from heat contents obtained through drop calorimetry. In general, there is good agreement between results of this study and those reported previously, despite the disparate techniques used in different studies. The largest disparities between the data of the present study and those obtained previously involve the data for dehydrated zeolites.

TABLE 4. Regressed Maier and Kelley (Eq. 3) coefficients describing the temperature dependence of C_P

Substance	a [J/(mol·K)]	$b \times 10^3$ (J/mol·K^2)	$c \times 10^{-5}$ (JK/mol)	T_{max} (K)
hydrated natrolite	279.69	452.8	−46.0513	403
dehydrated natrolite	266.26	221.6	−43.0155	633
hydrated analcime	77.017	361.7	24.2711	500
dehydrated analcime	141.02	151.9	−21.8203	633
wairakite	255.39	577.4	−23.5564	403
dehydrated wairakite	330.90	200.4	−67.7867	698

The data for dehydrated natrolite measured by Drebushchak (1990) are systematically higher than those obtained in this study, ranging from ~1% higher at room temperature to ~3% higher at 700 K. This may in part reflect the different compositions of the samples, as Drebushchak's (1990) sample had a composition ($Ca_{0.03}Na_{1.89}K_{0.02}Al_{1.97}Si_{3.03}O_{10}$) that deviates slightly from that of stoichiometric natrolite. However, adjustment of Drebushchak's (1990) data to a stoichiometric composition using an oxide sum algorithm (e.g., Helgeson et al. 1978; Ransom and Helgeson 1994) results in higher values of C_P (i.e., values that are less similar to those of the present study). More likely, the slightly non-stoichiometric formula reported by Drebushchak (1990) may reflect the presence of impurities, as natrolite is commonly found intergrown with related minerals (e.g., scolecite, gonnardite, thomsonite) that are more likely to contain Ca and K (Gottardi and Galli 1985). Such impurities could be the cause of the systematic discrepancy between our data and those of Drebushchak (1990), although the limited sample characterization reported in the previous study makes direct comparisons difficult. Also note that Drebushchak's (1990) data do not exhibit the N_2 desorption feature present in our data.

Our data for dehydrated analcime are systematically lower than those obtained by Johnson et al. (1982), King and Weller (1961), and Pankratz (1968) for samples with a composition nearly identical to our sample (see Johnson et al. 1982, for a discussion of the sample composition and resulting recalculation performed on the data of the previous studies). This discrepancy is unlikely to be caused by the minor compositional variation, as corrections to the previous data for composition by oxide summation algorithms results in even greater discrepancy. We feel that the underlying cause is likely the sample handling procedures used in previous studies. Although rehydration of analcime is very slow (cf. Chipera and Bish 1991; Neuhoff and Wang 2007), dehydrated analcime is very hygroscopic. Our fully dehydrated sample absorbed measurable quantities of H_2O from the air under ambient conditions after just a few hours exposure, which is why it was not exposed to humid air after dehydration and prior to measuring C_P. Although other studies by Johnson's group on dehydrated zeolites (e.g., Johnson et al. 1991, 1992) took significant measures to keep their samples isolated from water vapor during and after preparation of the dehydrated samples, similar procedures are not described by Johnson et al. (1982) or in the earlier studies of King and Weller (1961) and Pankratz (1968). As the specific heat of hydrated analcime is higher than that of dehydrated analcime (consistent with the C_P data in Tables 1–3), partial hydration of the analcime would result in calculated C_P values that are systematically too high, as found in this study. Because our sample was maintained in a completely dry atmosphere, and showed no evidence of dehydration during acquisition of DSC data for the dehydrated sample, it is most likely free from this potential complication. Consequently, we

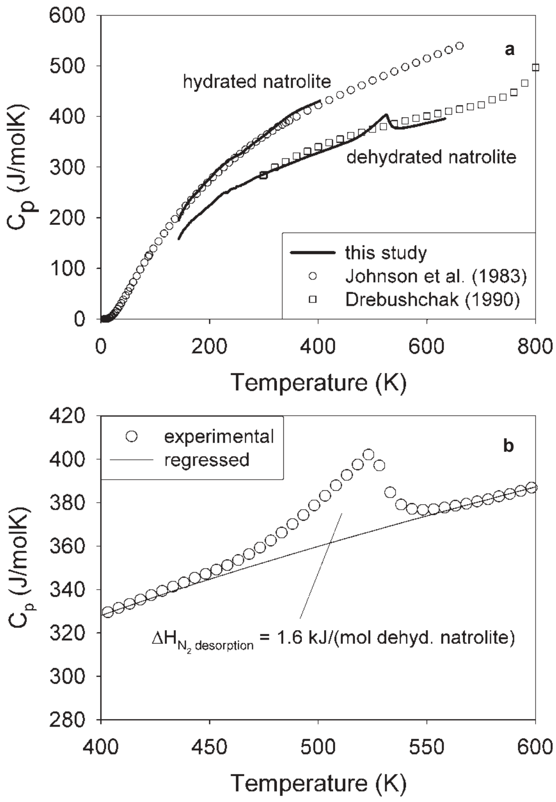

FIGURE 2. (**a**) Heat capacity of hydrated and dehydrated natrolite determined in this study (solid curves) as a function of temperature compared to previous results from Johnson et al. (1983) and Drebushchak (1990). (**b**) Comparison of measured C_P for dehydrated natrolite in this study in the region of the N_2 desorption peak with the regressed Maier and Kelley (1932; Eq. 2) fit to the C_P data outside of this anomaly (Table 4). Region between curves corresponds to the heat of desorption of N_2.

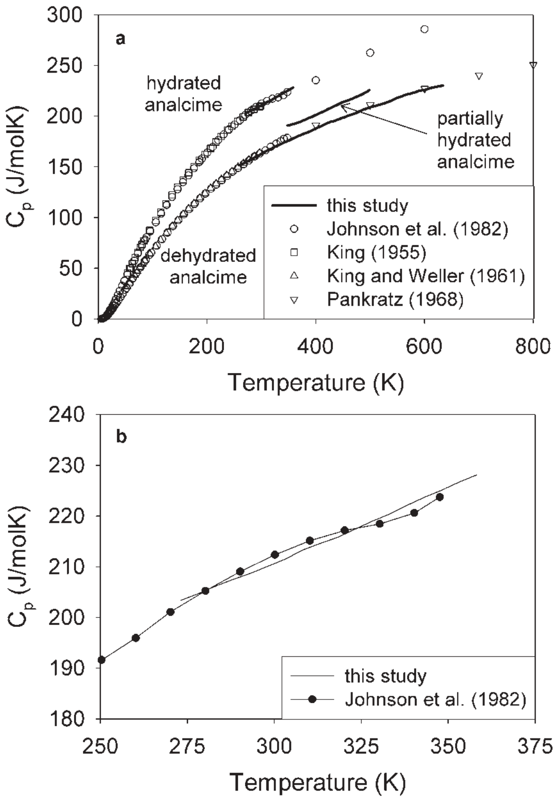

FIGURE 3. (**a**) Heat capacity of hydrated analcime, partially dehydrated analcime (see text), and dehydrated analcime determined in this study (solid curves) as a function of temperature compared to previous results from King (1955), King and Weller (1961), Pankratz (1968), and Johnson et al. (1982). Results from the literature have been corrected for the true water stoichiometry of the samples used (see text and Neuhoff et al. 2004). (**b**) Comparison of C_P results for hydrated analcime from the present study with the adiabatic calorimetric results of Johnson et al. (1982) in the region of the second-order phase transition in analcime.

adopt the C_P values for dehydrated analcime listed in Table 3 in the calculations below. Another potential explanation for this discrepancy lies in the indirect method by which C_P is assessed from drop calorimetric results. This is typically accomplished by fitting an integral form of the desired C_P polynomial (such as Eq. 3) to the heat content results by noting that, in the absence of any reactions, the enthalpy change of a sample associated with a change in temperature between the experimental temperature, T, and the reference temperature, 298.15 K ($H_{T\text{–}298.15}$), is given by

$$H_{T\text{–}298.15} = \int_{298.15}^{T} C_P \, \mathrm{d}T . \tag{4}$$

Thus, the temperature dependence of C_P is a sensitive function of the form of the polynomial used to fit the drop results, and may bias the data. Figure 5 shows $H_{T\text{–}298.15}$ calculated from the Maier and Kelley (1932) coefficients regressed from our results on dehydrated analcime (Table 4) compared to the drop calorimetric observations of Pankratz (1968). The heat contents calculated from our results are within 1% of those of Pankratz (1968) at all temperatures, suggesting that much of this discrepancy is an artifact of the fit obtained by Johnson et al. (1982) to their adiabatic data and those of Pankratz (1968). Note, however, that $H_{T\text{–}298.15}$ reported by Pankratz (1968) is systematically higher than our results, consistent with the suggestion that his sample may have been partially rehydrated.

To our knowledge, no quantitative C_P data have been reported previously for wairakite or dehydrated wairakite. Belitskii et al. (1993) provided a figure reporting specific heat data from ~315 to ~410 K for a hydrated wairakite sample from Wairakei, New Zealand that is compositionally similar to that used in the present study. Their data exhibit the same lambda-type anomaly as is apparent in our data (Fig. 1) although their specific heats are systematically higher than those of the present study by ~10%. Insufficient detail is provided to assess the cause of this discrepancy. Nonetheless, Belitskii et al. (1993) also observed that this transition is fully reversible, and provided XRD and thermomechanical data indicating that this transition involves an anomalous increase in thermal expansion during a change in symmetry from a polysynthetically twinned monoclinic phase at low temperature to a pseudocubic (tetragonal) phase at high temperature. This is similar to the second-order tetragonal to cubic transition observed in leucite (e.g., Lange et al. 1986; Palmer et al. 1989; Palmer and

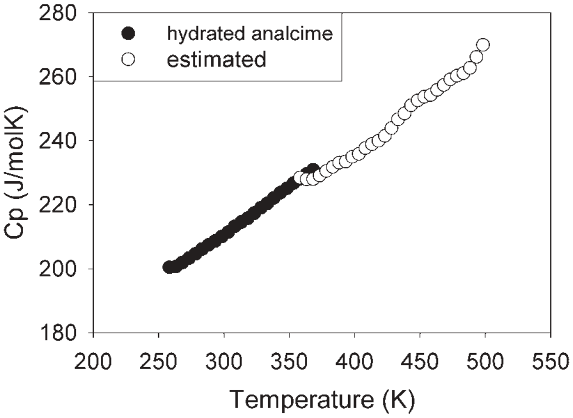

FIGURE 4. Measured C_P for hydrated analcime (black circles) compared to C_P for hydrated analcime estimated from the properties of partially hydrated analcime and dehydrated analcime via Equation 2 (open circles).

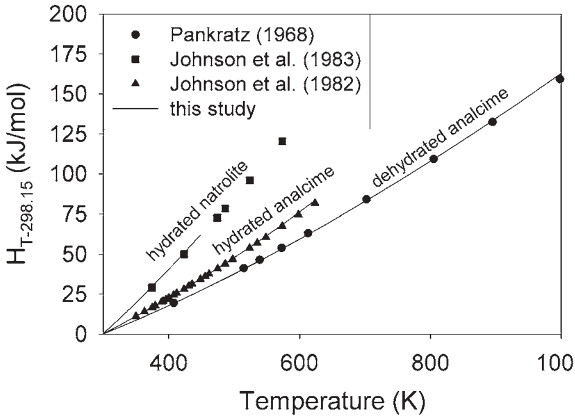

FIGURE 5. Comparison of enthalpy increments as a function of temperature ($H_{T\text{–}298.15}$) calculated from C_P results in this study to drop-calorimetric results of Johnson et al. (1982, 1983) and Pankratz (1968) for dehydrated analcime, hydrated natrolite, and hydrated analcime.

Salje 1990). As noted above, this transition in wairakite is not reflected in the C_P data for dehydrated wairakite.

The structural nature of the monoclinic to tetragonal transition in wairakite was recently investigated by Seryotkin et al. (2003) through in-situ single-crystal XRD measurements at elevated temperature. They found that the main structural feature of this transition involved a rearrangement of the water molecules leading to shortened H_2O–framework oxygen contact lengths associated with a distortion of the tetrahedral framework. The intimate association of this transition with the structural nature of water molecules is consistent with the C_P observations of the present study indicating that the transition is only present in the hydrated phase. The lack of a phase transition in the dehydrated phase suggests that the tetragonal symmetry noted in the dehydrated phase at elevated temperature by Seryotkin et al. (2003) is likely present at room temperature as well.

One striking aspect of the adiabatic C_P data for analcime reported by Johnson et al. (1982) is the presence of an anomaly that has been described as a "smeared lambda transition" (Ransom and Helgeson 1994) that results in a local maximum in C_P around 365 K (Fig. 3). Similar to the lambda transition noted in wairakite, this transition does not occur in the dehydrated form. Close inspection of our data (Fig. 3b) does not reveal the presence of this anomaly; rather, our C_P function represents a smoothed version of Johnson et al.'s (1982) C_P data that essentially coincide with their results at elevated temperatures.

One potential cause of this anomaly may be a symmetry change similar to that in wairakite. Hovis et al. (2002) predicted symmetry inversion temperature for analcime of 303–311 K based on comparison of room temperature and inversion temperature molar volumes of isostructural leucite-based materials. This prediction coincides nicely with the anomaly noted by Johnson et al. (1982). Analcime exhibits significant variations in its room-temperature symmetry between samples; Mazzi and Galli (1978) found examples with orthorhombic and tetragonal symmetry as well as cubic. The difference between the behavior of our sample and that of Johnson et al. (1982) may well be related to symmetry (neither has been the subject of a crystal structure refinement), with Johnson et al.'s (1982) sample having lower symmetry under subambient conditions that transforms to higher symmetry in the region of the anomaly shown in Figure 3. Potentially, our sample could exhibit a phase transition that is even more subdued in terms of C_P manifestation than that observed by Johnson et al. (1982). An alternative explanation may lie in the limitations of the DSC method, which requires that samples be heated quickly (in this case, 15 K/min) to obtain a signal. If the transitions in analcime are kinetically limited (which is likely the case in the temperature region of Fig. 3b), then the relatively fast heating rates employed may have caused the heat effects associated with this transition to have become smoothed out over a range of temperature. As shown below, however, the transition is evident in the data, though more subtly than implied by Johnson et al.'s (1982) data.

The veracity of C_P data derived from drop-alorimetric data for hydrated phases such as analcime and natrolite was questioned by Carey (1993), who noted that these materials may have dehydrated at elevated temperature and then rehydrate during the drop, resulting in heat content results that are higher than would result from the integral function in Equation 4 alone. The magnitude of this effect in the analcime and natrolite data of Johnson et al. (1982, 1983) can be assessed by comparing their drop results to $H_{T\text{–}298.15}$ calculated from the Maier and Kelley (1932) regression results presented in Table 4. This comparison is shown in Figure 5. It can be seen that in both cases, there is excellent agreement between the results of this study and those of Johnson et al. (1982, 1983). For both minerals, our results are within 1% of the drop-calorimetric measurements. This agreement indicates that the data of Johnson et al. (1982, 1983) are not affected by excess heat effects associated with rehydration, at least over the range of temperatures for which we were able to gather data. In the case of analcime, this holds true even over the range of temperatures in which our analcime sample dehydrated, and the regression presents the behavior of partially dehydrated analcime. The lack of dehydration and rehydration in Johnson et al.'s (1982, 1983) samples may be a consequence of the fact that any partial dehydration of the samples in the sealed ampoules used in their drop measurements would cause the partial pressure of water vapor to be high given the small amount of free space in the ampoule, thus preventing dehydration.

Heat capacities of hydration

In the absence of reliable calorimetric constraints on $\Delta C_{P(\mathrm{r})}$ for zeolite dehydration reactions over the range of temperature necessary to model the thermodynamic implications of phase-equilibrium observations, some workers have applied statistical-mechanical reasoning to estimate this property. Barrer (1978) reasoned that as water molecules change state during absorption of an ideal gas phase into the structure of a zeolite (or other absorbent), they experience a loss of rotational and translational degrees of freedom to vibrational modes in the crystal structure that should be manifested in an increase in the nominal C_P of the water molecule. This interpretation is consistent with experimental measurements of C_P for homologous hydrated and dehydrated zeolites (e.g., Basler and Lechert 1972; Johnson et al. 1982, 1991, 1992; Vučelić and Vučelić 1985; this study) that indicate a positive $\Delta C_{P(\mathrm{r})}$ for reaction 1. This theory further predicts that for each of the six degrees of motional freedom (three rotational and three translational) lost to vibrational modes in the crystal during sorption, C_P should increase by 0.5 R [where R is the gas constant, 8.314 J/(mol·K)] up to a maximum of 3R if all six degrees of freedom are lost. Baring phase transitions, $\Delta C_{P(\mathrm{r})}$ for reaction 1 should be invariant with temperature. Subsequently, several studies have assumed the temperature invariance of $\Delta C_{P(\mathrm{r})}$ predicted by this theory [using values of $\Delta C_{P(\mathrm{r})}$ derived from room C_P measurements at room temperature where dehydration is not a problem] to regress thermodynamic data from equilibrium observations at elevated temperatures with fair success (Carey and Bish 1996; Wilkin and Barnes 1999; Fridriksson et al. 2003; Fialips et al. 2005).

There are several potential problems with strict application of Barrer's (1978) statistical-mechanical model to reactions such as reaction 1. First, as most zeolites contain water molecules distributed over several crystallographically (cf. Mortier 1982; Armbruster and Gunter 2001) and energetically distinct sites (e.g., Fridriksson et al. 2003; Fialips et al. 2005), it seems reasonable that the number of degrees of freedom lost to vibrational modes may vary between water types in a given zeolite, causing $\Delta C_{P(\mathrm{r})}$ to deviate from the 0.5 R intervals suggested by this model depending on the relative abundance of the water molecules. This possibility would also suggest that site specific thermodynamic treatments of zeolite dehydration (e.g., Fridriksson et al. 2003; Fialips et al. 2005) may require different values of $\Delta C_{P(\mathrm{r})}$ for each water type in the model. Second, as noted by Carey (1993), phase transitions involving the water sites will cause $\Delta C_{P(\mathrm{r})}$ to vary with temperature. Third, the considerable contraction observed in some zeolite lattices during dehydration (Bish and Carey 2001) may lead to a significant change in the contribution of the framework to C_P between the hydrated and dehydrated forms. Lastly, it appears that in some zeolites, there may be excess heat capacity across the solid solution between the hydrated and dehydrated forms (Basler and Lechert 1972).

The zeolites used in this study all contain water molecules occupying either a single crystallographically distinct site or two sites that are crystallographically and energetically similar. Thus they are relatively free of potential complications arising from differential energetics of water molecules on distinct sites. The C_P results presented above were used to calculate $\Delta C_{P(\mathrm{r})}$ as a function of temperature, using values of C_P for steam consistent with the IAPWS95 formulation for water properties (Wagner and Pruss 2002) using the polynomial function of Cooper (1982). Raw C_P results were used for wairakite and natrolite, whereas the Maier and Kelley (1932) polynomial fits for analcime species were used for that phase. The results are shown in Figure 6, where $\Delta C_{P(\mathrm{r})}$ has been normalized to one mole of H_2O. The ticks and gridlines in Figure 6 are in increments of R for comparison with Barrer's (1978) model. It is clear from the results shown in Figure 6 that Barrer's (1978) statistical mechanical model does not readily explain the temperature dependence of $\Delta C_{P(\mathrm{r})}$ in these zeolites as all exhibit marked changes in $\Delta C_{P(\mathrm{r})}$ with temperature as a result of second-order phase transitions involving the water molecules.

In the case of analcime, $\Delta C_{P(\mathrm{r})}$ exhibits a minimum around 355 K (essentially the same temperature as suggested by Johnson et al. 1982) and increases continuously above this temperature. It should be noted that the shape of this curve may in part be an artifact of the fit coefficients regressed for analcime. However, the increase in $\Delta C_{P(\mathrm{r})}$ above 355 K is clearly indicated in the raw C_P measurements as well and the smeared lambda transition observed by Johnson et al. (1982) in analcime water nicely coincides with our curve. The continuous increase in $\Delta C_{P(\mathrm{r})}$ above 356 K may be associated with changes in the orientation and local bonding environment of water molecules with temperature (e.g., Line et al. 1994; Cruciani and Gualtieri 1999). Similar behavior was observed in clinoptilolite (Johnson et al. 1991), which led Carey (1993) to question the validity of drop calorimetric results on hydrated zeolites.

The behavior of natrolite and wairakite at low temperatures is consistent with a glass-type transition previously reported in phillipsite and the synthetic zeolites A and X (Haly 1972; Basler and Lechert 1972; Hemingway and Robie 1984; Vučelić and Vučelić1985). In natrolite, $\Delta C_{P(\mathrm{r})}$ increases continuously from 150 to 350 K (the sinusoidal variations in $\Delta C_{P(\mathrm{r})}$ are an artifact of noise in the low temperature C_P data that is accentuated in this calculation), and then becomes relatively insensitive to temperature. A similar transition is evident in wairakite between 175 and 300 K. It should be noted that this style of transition is common in confined water in nanopores over essentially the same temperature range as observed in wairakite (e.g., Mraw and Nass-O'Rourke 1979; Maruyama et al. 2004).

The monoclinic to tetragonal phase transition in wairakite between 350 and 500 K also has a dramatic effect on $\Delta C_{P(\mathrm{r})}$. Although this transition affects the framework symmetry and is thus not solely related to processes involving the water molecules, it is only present in the hydrated phase. Above 300 K, $\Delta C_{P(\mathrm{r})}$ increases regularly to a maximum at 425 K, at which point it decreases to 0 J/(mol·K). This value suggests that the water molecules in this phase become energetically similar to the ideal gas at elevated temperatures.

Implications for thermodynamic modeling of zeolite-water equilibria

Regression of thermodynamic data from observations of the equilibrium composition of zeolites as a function of temperature and water vapor pressure provides an important source of insight

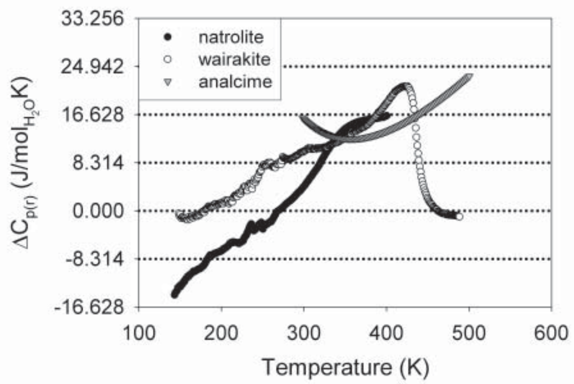

FIGURE 6. Calculated heat capacities of hydration per mole H_2O (cf. reaction 1) for analcime, natrolite, and wairakite calculated from the results of this study and C_P of steam from Cooper (1982).

into the energetics of zeolite-water systems (e.g., Bish and Carey 2001). These regressions typically require prior knowledge of $\Delta C_{P(r)}$, in part to minimize the number of variables being regressed (e.g., Bish and Carey 2001). This is usually done by making the assumption discussed above that $\Delta C_{P(r)}$ is temperature invariant (e.g., Carey and Bish 1996; Wilkin and Barnes 1999; Fridriksson et al. 2003; Fialips et al. 2005). The effect of this assumption on regressed thermodynamic properties can be assessed by calculating the integral change in the enthalpy and entropy of reaction due to a change in temperature, $\Delta H_{T\text{–}298.15(r)}$ and $\Delta S_{T\text{–}298.15(r)}$, respectively, given by

$$\Delta H_{T-298.15(r)} = \int_{298.15}^{T} \Delta C_{P(r)} \mathrm{d}T \tag{5}$$

and

$$\Delta S_{T-298.15(r)} \int_{298.15}^{T} \Delta C_{P(r)} \mathrm{dln}T \,. \tag{6}$$

Figure 7 shows the variation in $\Delta H_{T\text{–}298.15(r)}$ and $\Delta S_{T\text{–}298.15(r)}$ as a function of temperature calculated using the values of $\Delta C_{P(r)}$ generated in this study for analcime, natrolite, and wairakite. Shown for reference are the values obtained assuming that $\Delta C_{P(r)}$ is equal to R, 2R, and 3R.

The relationships depicted in Figure 7 illustrate the effect of temperature on the magnitude of errors associated with assumptions about the magnitude of $\Delta C_{P(r)}$. For instance, $\Delta C_{P(r)}$ is ~R at 298.15 K in both natrolite and wairakite, but increases to about 2R at 400 K (Fig. 6). Assuming that $\Delta C_{P(r)}$= R over this temperature range would only lead to errors in $\Delta H_{(r)}$ of ~500 J/mol and in $\Delta S_{(r)}$ of ~1 J/(mol·K). For comparison, typical values of $\Delta H_{(r)}$ and $\Delta S_{(r)}$ for zeolite hydration reactions from the gas phase are 60–100 kJ/mol and 100–200 J/(mol·K), respectively (Bish and Carey 2001). Thus, this error would be on the order of 1% or less, similar to or smaller than the errors typically attending the regression calculations themselves (cf. Carey and Bish 1996; Fialips et al. 2005). If $\Delta C_{P(r)}$ for natrolite is extrapolated to higher temperatures, however, the magnitude of this error will increase. The same reasoning holds true for wairakite through the temperature of its phase transition, at which point $\Delta H_{T\text{–}298.15(r)}$ and $\Delta S_{T\text{–}298.15(r)}$ become essentially invariant with temperature. In analcime, for which $\Delta C_{P(r)}$ = ~2R at 298.15 K, assuming that $\Delta C_{P(r)}$ is not a function of temperature leads to minimal errors through about 550 K, above which the increase in $\Delta C_{P(r)}$ with temperature leads to a progressively increasing difference in $\Delta H_{T\text{–}298.15(r)}$ and $\Delta S_{T\text{–}298.15(r)}$ with increasing temperature.

The net effect of the observations above is that assumptions of the magnitude of $\Delta C_{P(r)}$ have a relatively minor effect on thermodynamic properties regressed from experiments at relatively low temperatures, but the marked temperature dependence of $\Delta C_{P(r)}$ demonstrated in this study potentially leads to systematic errors in standard thermodynamic properties retrieved from equilibrium observations at relatively high temperatures. In particular, this may bias retrievals of site-specific properties, such as attempted by Fialips et al. (2005) in chabazite, or partial molar properties in phases that dehydrate over a protracted range of temperature, such as clinoptilolite (Carey and Bish 1996). In these cases, the energetics of water molecules that occur in the structures of zeolites at low degrees of hydration are regressed from experiments at relatively high temperatures, and may be subject to greater bias from assumed values of $\Delta C_{P(r)}$. In the case of materials like analcime and natrolite, for which $\Delta C_{P(r)}$ increases with increasing temperature, the effect will be to make the zeolitic water molecules appear less thermodynamically stable.

CONCLUDING REMARKS

The C_P data generated in this study provide important heuristic insights into the energetics of dehydration processes in zeolites. The demonstration that $\Delta C_{P(r)}$ is temperature dependent, and its relationship to the rich phase transition chemistry exhibited by zeolitic water molecules, underscores the need for quantitative measurement of C_P for mineral hydrates like zeolites in multiple states of hydration. Without such data, derivation and extrapolation of thermodynamic models based on calorimetric and phase-equilibrium observations is subject to error, particularly for experimental data collected at elevated temperatures. The simultaneous DSC-TGA methodologies employed in this study, in concert with adiabatic, heat pulse, and drop-calorimetric techniques, provides a useful means of acquiring such data.

In addition, the new C_P data generated in this study will facilitate consideration of the thermodynamic stability of analcime, natrolite, and wairakite in geologically relevant environments. The coincidence of the present results with those previously reported for hydrated analcime and natrolite (Johnson et al. 1982, 1983) should mitigate concerns in the literature about possible excess heat effects in the former results. Models of zeolite dehydration are critical for evaluating zeolite phase relations at elevated temperatures, as shown by Helgeson et al. (1978) for equilibria between analcime and the assemblage nepheline + albite. Detailed thermodynamic models of dehydration in both analcime and natrolite that incorporate the results of the present study are being developed by the authors to aid in these efforts. The results presented for wairakite are, to our knowledge, the first quantitative C_P measurements reported for this mineral. Although the present results do not extend to temperatures reported for equilibria involving wairakite (e.g., Liou 1970, 1971), they at least constrain the magnitude of C_P above the monoclinic-tetragonal phase transition. Thus, they should help resolve some of the ambiguities encountered in evaluating the thermodynamic properties of wairakite equilibria, which are subject to considerable

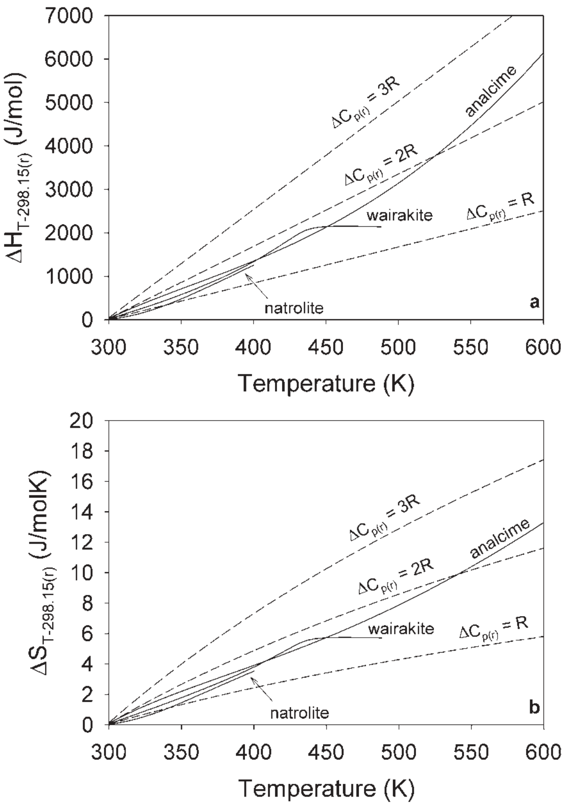

FIGURE 7. Calculated change in the enthalpy (**a**) and entropy (**b**) of reaction [$\Delta H_{T-298.15(r)}$ and $\Delta S_{T-298.15(r)}$, respectively] due to increasing temperature for analcime, natrolite, and wairakite calculated from the results of this study (solid curves). Shown for comparison are the same quantities calculated assuming that $\Delta C_{P(r)}$ is equal to R, 2R, and 3R.

inconsistencies between calculated and experimental Clapeyron slopes (e.g., Helgeson et al. 1978; Chipera and Apps 2001).

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