# Thermodynamics of dehydration in analcime: Absorption calorimetry and equilibrium observations

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# ABSTRACT

Analcime forms in a wide range of geologic environments from alkaline lakes to primary igneous occurrences in Si-undersaturated lavas and pegmatites and is present in many radioactive waste repository settings. To evaluate its hydration state in these environments, calorimetric-hydration heat measurements, equilibrium observations, and thermodynamic modeling were performed. The enthalpy of hydration of analcime determined by isothermal adsorption calorimetry was found to be independent of degree of hydration and relatively insensitive to temperature. Equilibrium hydration states of analcime as a function of temperature and vapor pressure were assessed by isothermal thermogravimetry. In light of the lack of excess enthalpy of mixing in this solution, an ideal solution model was applied to the equilibrium observations along with previously determined heat capacities hydration to retrieve the standard Gibbs energy of hydration from water vapor ( $-47.29 \pm 0.56$  kJ/ mol H<sub>2</sub>O), standard enthalpy of hydration ( $-85.10 \pm 1.03$  kJ/mol H<sub>2</sub>O), and entropy of hydration  $(-126.81 \pm 1.60 \text{ J/mol H}_2\text{O}\cdot\text{K})$  at 298.15 K, 1 bar. The standard enthalpy of hydration at 298.15 K, 1 bar regressed from the calorimetric data are consistent with these results ( $-86.4 \pm 1.9$  kJ/mol H<sub>2</sub>O). Calculations of the hydration state of analcime as a function of temperature and pressure indicate that analcime is essentially fully hydrated at temperature and pressure conditions attending its formation in geologic and experimental systems. Dehydration of analcime under water-undersaturated conditions (as during heating in a radioactive waste repository) may contribute significantly to thermal budgets in systems where this phase is important.

**Keywords:** Analcime, thermodynamics, hydration heat, dehydration, differential scanning calorimetry, thermogravimetry, equilibrium

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# INTRODUCTION

Analcime { $Na_rAl_rSi_{3-x}O_6$  [(3 - x)/2]H<sub>2</sub>O, where x varies from  $\sim 0.78$  to  $\sim 1.06$ } is one of the most common rock-forming zeolites. It forms over a considerable range of temperature and pressure conditions, spanning geologic environments from surficial conditions such as soils (e.g., Baldar and Whittig 1968; Bockheim and Ballard 1975; Hay 1978; Renaut 1993) and alkaline lakes (e.g., Hay 1986; de'Gennaro et al. 1990; Sheppard and Hay 2001) through diagenetic and low-grade metamorphic terranes (e.g., Coombs 1954; Wilkinson and Whetten 1964; Utada 1965; Boles 1991) to primary igneous occurrences in lavas and alkaline pegmatites (e.g., Pearce 1970; Woolley and Symes 1976; Luhr and Kyser 1989; Wilkinson and Hensel 1994; Neuhoff et al. 1997; Markl 2001). It is a useful indicator of physical conditions in the crust, often occurring in relatively narrow thermal windows in diagenetic and metamorphic systems (e.g., Iijima 1988; Walker 1960). In addition, the Si/Al ratio of analcime is sensitive to the chemical potential of silica, making it an important indicator of geochemical facies in near-surface environments (Wise 1984; Neuhoff et al. 2004).

The widespread occurrence and importance of analcime as a rock-forming mineral has led to numerous studies of its stability and thermodynamic properties. Recent focus on the stability of analcime during water-rock interaction in diagenetic and hydrothermal systems through solubility measurements and calorimetric studies (e.g., Apps 1970; Johnson et al. 1982; Murphy et al. 1996; Wilkin and Barnes 1998; Redkin and Hemley 2000) permitted Neuhoff et al. (2004) to develop an internally consistent thermodynamic model describing the stability of analcime solid solutions in these environments. In contrast, reconciliation of phase-equilibrium observations at elevated temperatures and pressures involving analcime (e.g., Greenwood 1961; Newton and Kennedy 1968; Manghnani 1970; Kim and Burley 1971; Liou 1971; Thompson 1971) has proven more difficult (cf. Thompson 1973). In large part, this is probably due to the complications arising from solid solution in analcime. In particular, Helgeson et al. (1978) demonstrated that coupled consideration of the consequences of Si/Al substitution and partial dehydration at elevated temperatures and pressures permits reconciliation of the numerous determinations of analcime phase equilibria reported in the literature. Helgeson et al. (1978) based these calculations on limited calorimetric observations of the thermodynamics of dehydration in analcime available at the time (e.g., King 1955; King and Weller 1961; Barany 1962) without the benefit of either calorimetric data or hydration state observations at elevated temperatures.

The present study investigates the thermodynamics of dehydration in analcime through a combination of calorimetric and equilibrium observations at elevated temperatures. Heats of hydration as a function of temperature determined by isothermal adsorption calorimetry are combined with observations of the equilibrium water content of analcime at elevated temperatures

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and vapor pressures to develop a thermodynamic model of analcime dehydration consistent with our recent determination of the heat capacity of dehydration in analcime (Neuhoff and Wang 2007b). These thermodynamic properties are then used to calculate the hydration state of analcime as a function of temperature and pressure and the thermal consequences of analcime dehydration in radioactive waste repositories.

## **EXPERIMENTAL METHODS**

#### Sample and characterization

The analcime sample was collected from a zeolite-facies metabasalt outcrop at Manillat on the island of Qeqertarssuaq in West Greenland (Neuhoff et al. 2003). A split of this sample was previously used and characterized by Neuhoff et al. (2003; Sample ANA002). A 1.5 cm euhedral crystal of opaque analcime was crushed and separates were hand picked, ground in an agate mortar, and sieved to the 20-40 µm size fraction. Sample purity and phase identity were confirmed by powder X-ray diffraction. Electron probe microanalysis indicated a composition of (NaAl)<sub>0.95</sub>Si<sub>2.05</sub>O<sub>6</sub>·1.025H<sub>2</sub>O, although the <sup>29</sup>Si magic angle spinning nuclear magnetic resonance (MAS NMR) results indicate a slightly less Si-rich composition of (NaAl)<sub>0.97</sub>Si<sub>2.03</sub>O<sub>6</sub>·1.015H<sub>2</sub>O. The latter value was chosen as more representative of the bulk composition (cf. Neuhoff et al. 2004). Water content of the sample was determined by thermogravimetric heating to 1023 K after the equilibration with a room temperature atmosphere of 50% relative humidity (RH), and the mass loss was measured to be  $8.29 \pm 0.03\%$  of the total sample. This value is within error of the water content calculated from the compositions determined by 29Si MAS NMR (8.32%; cf. Neuhoff et al. 2004). This latter value was adopted in this study, and all experimental data were evaluated assuming that the fully hydrated form of analcime in this study contained 1.015 mol of H2O per formula unit.

#### Calorimetry and thermogravimetry

All the experiments in this study were conducted on the Netzsch STA 449C Jupiter simultaneous thermal analysis system at the University of Florida. The core component of the system is a vacuum-tight, liquid-nitrogen-cooled furnace enclosing a sample carrier with thermocouples for measurement of temperature differences between the sample and a reference pan, generating a heat flux differential scanning calorimetric (DSC) signal. With respect to the present study, an essential aspect of this setup is that the DSC signal is measured simultaneously with thermogravimetric signals from a microbalance connected to the sample carrier. This allows the DSC signal to be interpreted directly in terms of water loss or gain to the sample as measured by thermogravimetric analysis (TGA).

Temperature and caloric calibrations were performed using data based on the DSC response of standard materials. A multipoint temperature calibration curve was developed using the melting points of H<sub>2</sub>O, Ga, In, Sn, Bi, Zn, and Al along with the solid-solid transition points of CsCl and quartz (Cammenga et al. 1993; Gmelin and Sarge 2000; Höhne et al. 1990; Sabbah et al. 1999). Because these materials are incompatible with the Pt-Rh crucible used in the experiments, temperature calibration was conducted in identical crucibles lined with a sub-millimeter thick insert of alumina. Caloric calibration was accomplished by the heat-flow rate method (Gmelin and Sarge 2000) using the DSC response of synthetic sapphire (Gmelin and Sarge 2000; Sabbah et al. 1999; Sarge et al. 1994; Stolen et al. 1996). The background-corrected DSC response of a synthetic sapphire disk similar in mass to the experimental charges was measured at heating rates of 5, 10, 15, and 20 K/min over the range of temperatures encountered in this study. Caloric calibration factors calculated from results at each heating rate agreed within 1% and were a nearly linear function of temperature.

Enthalpies of hydration of analcime as a function of temperature were determined using an isothermal DSC-based immersion technique (Neuhoff and Wang 2007a). This technique included two parts: complete dehydration by scanning heating and then rehydration under isothermal conditions. For each experiment, 20–30 mg of analcime sample were placed into a Pt-Rh crucible with unsealed, perforated lids. During the dehydration part, the system was evacuated under vacuum and then kept dry under ultra-pure N<sub>2</sub> with a constant flowing rate of  $\sim$ 50 mL/min. The sample was fully dehydrated by scanning heating from 298 to 873 K at the rate of 15 K/min and then allowed to cool to the experimental temperature. After equilibration (10–30 min) at this temperature under dry N<sub>2</sub> until both DSC and TGA baselines stabilized, the gas stream was changed to humidified N<sub>2</sub> that was generated by bubbling ultra-pure N<sub>2</sub> gas through a saturated NaCl solution (note that a dry protective gas stream was maintained at all times flowing into the base of the sample chamber to protect the balance; this gas mixes with the humidified gas resulting in a lower RH than that fixed by the solution). To reduce the change of DSC baseline, the flow rate of humidified gas was maintained at ~30 mL/min that resulted in an average water vapor pressure ( $P_{\rm H_{2O}}$ ) of 0.011–0.015 bar in the sample chamber during hydration steps (RH was monitored continuously on the gas stream exiting the system using a flow-through humidity meter manufactured by Sable Systems). Under this condition the sample was allowed to react until the DSC trace became relatively flat. Repeated experiments on one analcime sample gave virtually identical results, indicating that the sorption capacity and behavior of analcime was not affected by dehydration and rehydration. Consequently, some of the data at different temperatures were measured on the same sample aliquot.

The dehydration and rehydration behavior of analcime was studied by both scanning heating/cooling TGA and isothermal TGA under a humidified atmosphere. Scanning-heating TGA measurements were performed under a humid environment (~0.013 bar P<sub>H2O</sub>) at the heating/cooling rate of 2 K/min. Equilibrium water contents of analcime as a function of temperature and water vapor pressure were measured in isothermal, constant vapor pressure TGA experiments at  $P_{\rm H20}$  of ~0.009, 0.013, and 0.017 bar. To generate higher P<sub>H20</sub> (~0.017 bar), a non-saturated NaCl solution (~2.5 m) was used instead for gas bubbling in some of the experiments. Water vapor pressure was adjusted by mixing the humidified gas stream with dry N2. The analcime sample was heated to the experimental temperature rapidly (at 30 K/min) in the presence of humidified gas, and then kept under this condition until both the TGA and DSC signals decayed to baseline and became stable, indicating completion of reaction. True experimental reversals (i.e., determination of the equilibrium water content via hydration) were not possible due to the much slower kinetics of the hydration reactions. Nonetheless, the simultaneous monitoring of both the DSC and TGA signals with time provides a very sensitive test of completeness of reaction during dehydration. Mass changes recorded by the TGA signal were used to calculate the equilibrium water content of analcime at each temperature. The background correction of the TGA data was conducted by measuring the mass change of an empty crucible as a function of temperature. Uncertainties in sample mass associated with background and sample measurements were ~0.01 mg, and were propagated through the calculation of end-member mole fractions for assessment of errors. As discussed below, hydration and dehydration of analcime is very slow, even at elevated temperatures, which essentially precluded equilibrium observations below about 550 K.

# RESULTS

#### Isothermal hydration heat measurements

The behavior of analcime during isothermal hydration heat measurements has been discussed in detail by Neuhoff and Wang (2007a) and thus will only be described briefly here. An example of analcime isothermal hydration at 403 K is shown in Figure 1. After introduction of water vapor, the sample immediately started to absorb water, leading to abrupt changes in both the DSC and TGA signals. It is observed that the hydration of analcime is initially relatively rapid (as shown by the peak in the first derivative of the TGA signal, dTGA) and then decays exponentially. After about 150 min of reaction with the humid atmosphere, the reaction slows to a point where the DSC signal has decayed to near baseline level and is essentially invariant with respect to time even though sample continued to absorb  $H_2O$  (as evidenced by the gradual increase in the TGA signal). The slow rate of the reaction is also reflected in the near-zero value of dTGA.

The slow rate of rehydration exhibited by analcime in these experiments (and noted previously; Chipera and Bish 1991) does not allow for complete rehydration and thus precludes direct quantification of total integral enthalpies of hydration. For instance, during the experiment shown in Figure 1, the sample reabsorbed <2% of its mass before the DSC signal became indistinguishable from the baseline, as opposed to ~9.1% mass gain for complete rehydration. Consequently, in a strict sense



**FIGURE 1.** Example of isothermal immersion experiment on analcime at 403 K showing simultaneously recorded TGA and DSC signals for analcime as a function of time. The first derivative of the TG curve is given by the curve labeled dTGA. Region of the gray box denotes initial equilibration of sample at experimental temperature under dry N<sub>2</sub>. The rest of the experiment was conducted in the presence of a flow of humidified N<sub>2</sub> ( $P_{\rm H_{20}} = \sim 0.012$  bar).

only partial molar enthalpies of hydration ( $\Delta \overline{H}_{R,TP}$ ) for analcime were derived from these experiments. Two methods were thus employed to calculate  $\Delta \overline{H}_{R,T,P}$  following the approaches outlined in Neuhoff and Wang (2007a). The first is based on the fact that the DSC and dTGA signals in Figure 1 exhibit strikingly similar curve shapes, suggesting that these signals are strongly and linearly correlated. Thus, the dependence of the DSC signal on the dTGA signal was determined by linear regression to calculate the average  $\Delta \overline{H}_{R,T,P}$  (corresponding to the slope of the regression) and the baseline level of the DSC signal (the intercept of the regression line representing the DSC signal at dTGA = 0). Large uncertainties are usually associated with  $\Delta \overline{H}_{R,TP}$  calculated in this way due to the oscillation of DSC and dTGA signals. To overcome this, a second method was employed that used the DSC baseline determined from the linear regression of the DSC and dTGA signals to reevaluate the DSC data in terms of the

TABLE 1. Partial molar enthalpy of hydration of analcime



**FIGURE 2.** Cumulative heat evolved during absorption of water into analcime as a function of mass absorbed calculated from the experimental data shown in Figure 1. The slope of the data, which is linear over the range of compositions achieved during this experiment, defines  $\Delta \overline{H}_{R,T,P}$  (-84.41 kJ/mol H<sub>2</sub>O).

cumulative heat evolved during the course of rehydration as a function of mass absorbed (Fig. 2). It can be seen that the baseline corrected cumulative area under the DSC curve and the amount of absorbed H<sub>2</sub>O are highly correlated ( $R^2$  indistinguishable from 1.0). This result indicates that  $\Delta \overline{H}_{R,TP}$  is independent of the degree of hydration over the range of hydration states attained in this experiment (as well as all others listed in Table 1). The slope of the regression line in Figure 2 thus corresponds to the  $\Delta \overline{H}_{R,TP}$ . Using both methods outlined above,  $\Delta \overline{H}_{R,TP}$  was calculated from experimental observations at various temperatures (Table 1). Attempts were made to acquire usable data at temperatures <400 K and >470 K. However, below 400 K, absorption of water was too slow to allow reliable quantification of the results. It can be seen from the water contents and experimental durations reported in Table 1 that temperature generally promoted advancement of

Т (К)	m <sub>sample</sub> (mg)	Duration* (min)	Water uptake†	$\Delta \overline{H}_{R,T,P}$ ‡ (kJ/mol H <sub>2</sub> O)	$\Delta \overline{H}_{R,T,P}$ § (kJ/mol H <sub>2</sub> O)	$\Delta \overline{H}_{R,T,P}$ (kJ/mol H <sub>2</sub> O)
403.15	29.60	95	0.21	-84.67	-84.41	-84.72±1.73
	22.93	73	0.18	-85.68	-85.53	
	25.67	97	0.21	-84.34	-83.71	
417.15	25.67	82	0.24	-84.21	-84.63	$-84.42 \pm 1.10$
	27.46	83	0.25	-84.85	-84.67	
	29.13	110	0.26	-83.93	-84.20	
432.15	22.93	110	0.31	-83.81	-84.05	-84.10±1.13
	25.67	100	0.31	-83.79	-83.83	
	29.13	100	0.34	-84.38	-84.71	
446.15	22.91	150	0.41	-84.59	-84.45	$-84.84 \pm 1.49$
	22.93	69	0.29	-84.08	-84.40	
	29.14	74	0.31	-85.38	-85.63	
	29.13	115	0.34	-84.88	-85.33	
463.15	22.93	79	0.36	-84.38	-84.56	$-84.45 \pm 1.29$
	29.14	84	0.37	-83.50	-83.71	
	29.13	100	0.37	-84.41	-84.70	
	29.60	108	0.40	-85.19	-85.17	
470.15	25.67	110	0.39	-85.07	-84.23	$-84.14 \pm 2.04$
	27.76	260	0.48	-83.70	-83.54	

\* Duration of immersion portion of experiment used in data regression.

+ Fractional water content after rehydration.

<sup>‡</sup> Partial molar enthalpy of hydration in analcime calculated by linear regression of DSC and dTGA (see text).

§ Partial molar enthalpy of hydration in analcime calculated from cumulative, baseline-corrected DSC and mass of absorbed H<sub>2</sub>O (see text).

the reaction due to faster kinetics. However, above 470 K, the limited water sorption capacity of analcime at the vapor pressures of these experiments (see below) cancelled out this effect and precluded quantification of the results. Results from both methods of calculating partial molar enthalpy were in good agreement with each other, and were averaged across all experiments at a given temperature to give the values and errors listed in the last column of Table 1. The temperature dependence of  $\Delta \overline{H}_{R,T,P}$  is shown in Figure 3, where it can be seen that, within error,  $\Delta \overline{H}_{R,T,P}$  is insensitive to temperature from 403 to 470 K.

#### Hydration state as a function of temperature

Figure 4 shows the results of dynamic heating and cooling TGA measurements of analcime hydration state as a function of temperature at ~0.013 bar. During heating, analcime continually loses mass until fully dehydrated (~773 K). Upon cooling in a humid atmosphere, it partially rehydrates (~46%) when cooled back to 298 K. The heating and cooling curves are thus not coincident. Although not shown in Figure 4, TGA experiments at various heating rates indicate that the difference between the heating and cooling curves increases with increased heating rate. This fact, in combination with the rate observations detailed above and the increasing separation between the heating and cooling curves in Figure 4 with decreasing temperature, indicate that the hydration states achieved during scanning-heating/cooling experiments are kinetically controlled and thus are not suitable for retrieval of thermodynamic data.

Equilibrium observations of analcime hydration state measured by isothermal thermogravimetry are listed in Table 2 as a function of temperature and  $P_{\rm H_20}$ . These observations were limited to temperatures above 550 K due to the kinetic limitations. The experiments conducted below 550 K did not attain equilibrium at reasonable time scales, which resulted in the lack of high water content data in our equilibrium observations. The results at ~0.013 bar  $P_{\rm H_20}$  are compared to the dynamic TGA data



**FIGURE 3.** Enthalpy of hydration of analcime as a function of temperature. Solid circles show the  $\Delta H_{R,T,P}$  calculated from isothermal immersion experiments (Table 1) and the empty circle shows the  $\Delta H_{R,T,ref,P_{ref}}^{o}$  regressed from equilibrium data in this study. Shown for comparison are previous determinations of the enthalpy of hydration from Barany (1962), Johnson et al. (1982), Ogorodova et al. (1996), and van Reeuwijk (1974). The solid curve and dashed curve depict  $\Delta H_{R,T,P}^{o}$  as a function of temperature regressed from the calorimetric and equilibrium observations of this study, respectively.

in Figure 4. It can be seen that these data fall between the two dynamic TGA curves, consistent with the kinetic interpretation of the difference between the scanning heating and cooling curves. The data at all three pressures are presented in Figure 5, showing that the water content of analcime is a continuous function of both temperature and  $P_{\rm H20}$ .

# THERMODYNAMIC ANALYSIS

The dehydration of the analcime sample used in this study can be represented by the chemical equation:



**FIGURE 4.** Water content of analcime at  $P_{\rm H_{20}}$  of ~0.013 bar as a function of temperature (circles) compared to previous results from Balgord and Roy (1973; triangles) at 0.010 bar. Shown for comparison are the results of scanning heating/cooling TGA measurements at heating/ cooling rates of 2 K/min and the equilibrium water content of analcime calculated from the thermodynamic model of this study.

 TABLE 2. Equilibrium water contents of analcime as a function of

T (K)	P <sub>H2</sub> 0 (bar)	$X_{ m hydrated\ analcime}$	In <i>K</i> *		
553.15	0.009	0.2175 ± 0.0075	$-3.5012 \pm 0.0448$		
573.15	0.009	$0.1406 \pm 0.0047$	$-2.9711 \pm 0.0394$		
573.15	0.013	$0.1899 \pm 0.0055$	$-2.9573 \pm 0.0359$		
573.15	0.017	$0.2159 \pm 0.0048$	$-2.8461 \pm 0.0286$		
593.15	0.009	$0.0877 \pm 0.0051$	$-2.4396 \pm 0.0658$		
593.15	0.013	$0.1250 \pm 0.0055$	$-2.4620 \pm 0.0508$		
593.15	0.017	$0.1546 \pm 0.0055$	$-2.4370 \pm 0.0428$		
613.15	0.009	$0.0505 \pm 0.0068$	$-1.8468 \pm 0.1510$		
613.15	0.012	$0.0793 \pm 0.0076$	$-2.0377 \pm 0.1095$		
613.15	0.017	$0.1005 \pm 0.0077$	$-1.9445 \pm 0.0884$		
632.15	0.009	$0.0276 \pm 0.0087$	$-1.2209 \pm 0.3868$		
632.15	0.012	$0.0505 \pm 0.0098$	$-1.5548 \pm 0.2266$		
632.15	0.017	$0.0669 \pm 0.0106$	$-1.5003 \pm 0.1841$		
652.15	0.009	$0.0192 \pm 0.0087$	$-0.8494 \pm 0.6110$		
652.15	0.012	$0.0337 \pm 0.0098$	$-1.1318 \pm 0.3552$		
652.15	0.017	$0.0405 \pm 0.0106$	$-0.9693 \pm 0.3154$		
671.15	0.009	$0.0120 \pm 0.0084$	$-0.3720 \pm 1.2029$		
671.15	0.014	$0.0228 \pm 0.0088$	$-0.5764 \pm 0.4922$		
671.15	0.017	$0.0272 \pm 0.0106$	$-0.5599 \pm 0.5049$		
691.15	0.009	$0.0084 \pm 0.0061$	$-0.0117 \pm 1.2764$		
691.15	0.015	$0.0168 \pm 0.0063$	$-0.1949 \pm 0.4774$		
691.15	0.017	$0.0188 \pm 0.0077$	$-0.1817 \pm 0.5311$		
710.15	0.009	$0.0048 \pm 0.0046$	$0.5515 \pm 3.0705$		
710.15	0.015	$0.0120 \pm 0.0044$	$0.1465 \pm 0.4571$		
710.15	0.017	$0.0140 \pm 0.0045$	$0.1182 \pm 0.3933$		
730.15	0.009	$0.0036 \pm 0.0034$	$0.8404 \pm 4.4866$		
730.15	0.015	$0.0096 \pm 0.0036$	$0.3720 \pm 0.4403$		
730.15	0.017	$0.0104 \pm 0.0035$	$0.4194 \pm 0.4151$		
750.15	0.009	$0.0012 \pm 0.0012$	$1.9414 \pm 4.6144$		
750.15	0.014	$0.0048 \pm 0.0015$	$1.0000 \pm 0.3818$		
750.15	0.017	$0.0080 \pm 0.0015$	0.6846 ± 0.2098		
*Errors are asymmetrical; value listed is larger error.					

$$\begin{split} &Na_{0.97}Al_{0.97}Si_{2.03}O_{6}\cdot 1.015H_{2}O = Na_{0.97}Al_{0.97}Si_{2.03}O_{6} \\ &+ 1.015\ H_{2}O_{vapor}. \end{split}$$

#### Analcime-dehydrated analcime

Congruent with the conventions typically adopted for minerals, the standard state for the mineral components of reaction 1 is unit activity of the pure component at all temperatures and pressures. The standard state adopted for water vapor is unit fugacity of the ideal gas at 1 bar and any temperature. Calculations below involving liquid water employ a standard state of unit activity of the pure phase at all temperatures and pressures. The equilibrium constant (*K*) for reaction 1 may be written as:

$$\log K = 1.015 \log f_{\rm H_2Ovapor} + \log a_{\rm dehydrated analcime} - \log a_{\rm hydrated analcime}$$
(2)

where  $f_{\text{H}_2\text{Ovapor}}$  is the fugacity of water vapor, and *a* refers to the activities of the subscripted mineral components.

The equilibrium constant at temperature (*T*) and pressure (*P*) is related to the standard Gibbs energy of reaction at *T* and  $P(\Delta G_{R,T,P}^{\circ})$  by

$$\Delta G_{R,T,P}^{\circ} = -RT \ln K_{T,P} \tag{3}$$

where R is the gas constant;  $\Delta G^{\circ}_{R,T,P}$  is related to the standard enthalpy and entropy of reaction at T and P ( $\Delta H^{\circ}_{R,T,P}$  and  $\Delta S^{\circ}_{R,T,P}$ , respectively) by

$$\Delta G_{\mathrm{R},T,P}^{\circ} = \Delta H_{\mathrm{R},T,P}^{\circ} - T \Delta S_{\mathrm{R},T,P}^{\circ}.$$
<sup>(4)</sup>

The properties of the reaction in Equation 4 at elevated temperatures and pressures can be evaluated from the corresponding properties at the reference temperature ( $T_{ref}$ , 298.15 K) and pressure ( $P_{ref}$ , 1 bar) via the relationships:

$$\Delta G^{\circ}_{\mathrm{R},T,P} = \Delta G^{\circ}_{\mathrm{R},T_{\mathrm{st}},P_{\mathrm{st}}} - \Delta S^{\circ}_{\mathrm{R},T_{\mathrm{st}},P_{\mathrm{st}}}(T - T_{\mathrm{ref}}) +$$
(5)  
$$\int_{T_{\mathrm{st}}}^{T} \Delta C^{\circ}_{P,\mathrm{R}} dT - T \int_{T_{\mathrm{st}}}^{T} \Delta C^{\circ}_{P,\mathrm{R}} d\ln T + \int_{P_{\mathrm{st}}}^{P} \Delta V^{\circ}_{\mathrm{R}} dP ,$$
$$\Delta H^{\circ}_{\mathrm{R},T,P} = \Delta H^{\circ}_{\mathrm{R},T_{\mathrm{st}},P_{\mathrm{st}}} + \int_{T_{\mathrm{st}}}^{T} \Delta C^{\circ}_{P,\mathrm{R}} dT ,$$
(6)

and

$$\Delta S_{\mathrm{R},T,P}^{\mathrm{o}} = \Delta S_{\mathrm{R},T_{\mathrm{nf}},P_{\mathrm{nf}}}^{\mathrm{o}} + \int_{T_{\mathrm{nf}}}^{T} \Delta C_{P,\mathrm{R}}^{\mathrm{o}} d\ln T$$
(7)

where  $\Delta C_{P,R}^{\circ}$  is the standard heat capacity of reaction, and  $\Delta V_{R}^{\circ}$  is the standard volume of reaction.

Evaluation of standard thermodynamic properties for reaction 1 from the equilibrium observations presented above requires a model relating the proportions of the hydrated and dehydrated components in analcime to their respective activities. Several lines of evidence suggest that mixing between hydrated and dehydrated analcime is essentially ideal. First, water molecules occupy only one crystallographic site in analcime (e.g., Mazzi and Galli 1978; Cruciani and Gualtieri 1999), which generally would limit interactions leading to non-ideal behavior (especially excess-entropy contributions). More importantly, calorimetric observations indicate ideal enthalpic behavior in analcimedehydrated analcime solid solutions. Although the calorimetric observations of this study pertain to only a limited range of solid solution, the invariance of  $\Delta H^o_{R,T,P}$  with degree of hydration suggests that no excess enthalpy of mixing ( $H^{EX}$ ) is present. This is congruent with the findings of Ogorodova et al. (1996) who determined the enthalpy of formation ( $\Delta H_f$ ) of analcime across the whole solution between the hydrated and dehydrated form and found that this property was a linear function of composition. Consequently, in the calculations described below,  $a_{dehydrated analcime}$  and  $a_{hydrated analcime}$  were taken to be equivalent to their respective mole fractions ( $X_i$ ) as determined by TGA.

Evaluation of the thermodynamic properties of reaction 1 was based on regression of the equilibrium observations presented above. The calorimetric observations of  $\Delta H^{\circ}_{R,T,P}$  presented in Table 1 were not used as part of the regression due to the relatively large errors attending these measurements. However, both the ideal solution behavior and the consistency between  $\Delta C_{P,r}^{\circ}$  determined by Neuhoff and Wang (2007b) and the temperature dependence of the calorimetric  $\Delta H^{\circ}_{r,T,P}$  data both were used as heuristic insights in developing the regression model. The equilibrium observations presented above were recast as equilibrium constants for the purposes of regressing values of  $\Delta G^{\circ}_{R,T_{ref},P_{ref}}$ ,  $\Delta H^{\circ}_{R,T_{ref},P_{ref}}$ , and  $\Delta S^{\circ}_{R,T_{\text{ref}},P_{\text{ref}}}$  Calculated values of ln K are listed in Table 2 and plotted as a function of reciprocal of temperature in Figure 6. It can be seen in Table 2 and Figure 6 that ln K obtained at a given temperature but different  $P_{\rm H20}$  are within error of each other, consistent with the ideal solution model described above. The relatively larger errors in ln K associated with the higher temperature data are a consequence of larger relative errors in  $X_i$ at very low hydration states. It can be seen in Figure 6 that ln K for reaction 1 increases with increasing temperature, consistent with the positive  $\Delta \overline{H}_{R,TP}$  of reaction 1 determined above.

The temperature and pressure integrals in Equation 5 were evaluated with the aid of previously reported  $C_P^{\circ}$  and  $V^{\circ}$  data for the phases in reaction 1. The temperature dependence of  $C_P^{\circ}$  was represented by the Maier and Kelley (1932) equation

$$C_P^{\circ} = a + bT + cT^{-2}.$$
 (8)

The change in heat capacity across reaction 1 was calculated as a function of temperature based on  $C_P^{\circ}$  of hydrated and dehydrated analcime reported by Neuhoff and Wang (2007b) and  $C_P^{\circ}$  of water vapor as represented by the polynomial equation of Cooper (1982; Table 3). It should be noted that the  $C_P^{\circ}$  observations reported by Neuhoff and Wang (2007b) extend only to ~500 K due to difficulties arising from dehydration of analcime at more elevated temperatures. However, the consistency of these

**TABLE 3.** Maier and Kelley (1932) coefficients describing the temperature dependence of  $C_{P}^{\rho}$  (cf. Eq. 8)

Substance	a (J/mol·K)	b × 103 (J/mol·K2)	c × 10 <sup>-5</sup> (J⋅K/mol)		
Hydrated analcime*	77.017	361.7	24.2711		
Dehydrated analcime*	141.020	151.9	-21.8203		
Steam†	27.978	13.1	1.6560		
$\Delta C_{P,R}^{\circ}$	91.035	-193.6	-43.7542		

\* Neuhoff and Wang (2007b).

† Regressed from values calculated using the polynomial equation of Cooper (1982).



**FIGURE 5.** Mole fraction of hydrated analcime ( $X_{hydrated analcime}$ ) as a function of temperature and  $P_{H_{2O}}$ . Symbols correspond to observations listed in Table 2. Curves represent calculated (cf. Equations 2 to 7) equilibrium water contents at  $P_{H_{2O}}$  approximating the conditions of the equilibrium experiments.

results with those reported by Johnson et al. (1982), which are valid up to ~623 K, suggests that they may be applied up to at least this temperature. To include the equilibrium observations at temperatures above 623 K listed in Table 2 in the regression calculations, the Maier and Kelley (1932) coefficients listed in Table 3 were used to evaluate the temperature dependence of  $\Delta C_{P,R}^{o}$  at higher temperatures. The volume change reaction 1 was calculated from unit-cell volume volumes of hydrated (Gottardi and Galli 1985) and dehydrated (Putnis et al. 1993) analcime at 1 bar, and corresponds to 1.2 cm<sup>3</sup>/mol.

Values of  $\Delta G^{\circ}_{R, T_{\text{ref}}, P_{\text{ref}}}$ ,  $\Delta H^{\circ}_{R, T_{\text{ref}}, P_{\text{ref}}}$ , and  $\Delta S^{\circ}_{R, T_{\text{ref}}, P_{\text{ref}}}$  were regressed from the data presented in Table 2 and Figure 6 combining Equations 3, 4, 5, and 8. Explicit evaluations of the temperature integrals in Equation 5 were combined with values of  $\Delta H_{RTP}^{\circ}$ calculated from the data in Table 2 via Equation 3 to reduce Equation 5 to a linear equation in temperature. This yielded values of  $\Delta G^{\circ}_{R,T_{\text{ref}},P_{\text{ref}}}$  and  $\Delta S^{\circ}_{R,T_{\text{ref}},P_{\text{ref}}}$  consistent with the curve in Figure 6. The values of  $\Delta G^{\circ}_{R,T_{\text{ref}},P_{\text{ref}}}$  and  $\Delta S^{\circ}_{R,T_{\text{ref}},P_{\text{ref}}}$  obtained by linear regression are then used to calculate  $\Delta H^{\circ}_{R,T_{ref},P_{ref}}$  through Equation 4. The retrieved values were given in Table 4. Also shown in Table 4 is  $\Delta H^{\circ}_{R,T_{ref},P_{ref}}$  regressed from the data presented in Table 1 using the Maier and Kelley (1932) coefficients in Table 3. The temperature dependence of  $\Delta H_{R,T,P}^{o}$  consistent with both the calorimetric data and equilibrium observations are compared in Figure 3. It can be seen in Table 4 and Figure 3 that the calorimetric data indicate values of  $\Delta H^{\circ}_{BTP}$  that are somewhat lower, but generally within error, of those retrieved from the equilibrium observations.

#### DISCUSSION

#### Comparison with previous results

The standard enthalpies of hydration of analcime at 298.15 K derived from both calorimetry and equilibrium observations are compared to previous determination in Table 4 and Figure 3. Johnson et al. (1982) and Barany (1962) determined  $\Delta H_{R,T,P}^{\circ}$  by measuring the enthalpies of solution for pairs of homologous hydrated and dehydrated analcimes by HF solution calorimetry (note that the samples used in both studies had essentially iden-



**FIGURE 6.** Calculated equilibrium constant of reaction 1 as a function of temperature based on data presented in Table 2 (symbols). Curve represents the calculated temperature dependence of  $\ln K$  at 1 bar consistent with Equations 2 through 7 and the thermodynamic properties listed in Table 3.

tical compositions). The value of  $\Delta H_{R,Tref,Pref}^{o}$  from Ogorodova et al. (1996) was generated by transposed-temperature drop calorimetry. The results of Ogorodova et al. (1996) and Johnson et al. (1982) are quite close to that obtained in our study (<1% discrepancy) despite the fact that these three values were obtained by three independent techniques. Only the calorimetric data of Barany (1962) are inconsistent with this trend, being significantly less exothermic. The cause of this discrepancy is unclear (note that the value listed in Table 4 and shown in Fig. 3 were recalculated by Johnson et al. 1982 to account for outdated reaction properties in the thermochemical cycle used by Barany 1962). The consistency among all of the more recent data (including those of this study) suggests that the datum of Barany (1962) is likely in error.

As discussed above,  $\Delta \overline{H}_{R,T,P}$  of analcime is independent of the degree of hydration, leading to ideal solution between the hydrated and dehydrated end-members. Consequently,  $\Delta \overline{H}_{R,T,P}$ and  $\Delta H^{\circ}_{R,T,P}$  should be equivalent for analcime hydration under the same experimental conditions. Thus, the  $\Delta \overline{H}_{R,T,P}$  observations made in this study can be directly compared in magnitude with  $\Delta H^{\circ}_{R,T,P}$  determined through calorimetry or thermodynamic regression of equilibrium observations. This comparison is made in Figure 3, where the  $\Delta H^{\circ}_{R,T,P}$  results discussed above are compared as a function of temperature to the  $\Delta \overline{H}_{R,T,P}$  data in Table 1 and  $\Delta H^{\circ}_{R,T,P}$  at higher temperature (i.e., 569.15 K) retrieved from the phase-equilibrium observations by van Reeuwijk (1974). Despite the wide range of temperature and the various techniques pertinent to the data in Figure 3, there is generally excellent agreement between studies.

The relatively small change of  $\Delta H^{\circ}_{R,T,P}$  with temperature shown in Figure 3 is consistent with our previous observations of the magnitude of  $\Delta C^{\circ}_{PR}$  (Neuhoff and Wang 2007b). Taken as a whole, the data shown in Figure 3 suggest an increase in  $\Delta H^{\circ}_{R,T,P}$ between 400 and 470 K of <1 kJ/mol up to a maximum of ~3.2 kJ/mol if the errors are taken into consideration. The integral of the  $\Delta C^{\circ}_{P,R}$  over this temperature corresponds to 1.2 kJ/mol. This coincidence is shown in Figure 3 by the excellent agreement between the temperature dependence of  $\Delta H^{\circ}_{R,T,P}$  exhibited by the immersion calorimetric results and the regressed curve based on the Maier and Kelley (1932) coefficients listed in Table 3.

<b>The H</b> , Standard thermodynamic properties of analeme hydration						
	<i>T</i> (K)	$\Delta G^{\circ}_{R,T_{ref},P_{ref}}$ (kJ/mol H <sub>2</sub> O)	$\Delta H^{\circ}_{R,T_{ref},P_{ref}}$ (kJ/mol H <sub>2</sub> O)	$\Delta S^{\circ}_{R,T_{ref},P_{ref}}$ (J/mol H <sub>2</sub> O·K)	$\Delta V_{\text{R,T}_{\text{ref}},P_{\text{ref}}}^{\circ}$ (cm <sup>3</sup> /mol H <sub>2</sub> O)	
This study*	298.15		-86.40 ± 1.90			
This study†	298.15	$-47.29 \pm 0.56$	-85.10 ± 1.03	$-126.81 \pm 1.60$	1.2	
Johnson et al. (1982)	298.15	$-44.9 \pm 4.8$	$-84.9 \pm 4.8$	$-133.76 \pm 0.29$		
Bish and Carey (2001)‡	298.15	-43.5	-80.4	-123.7		
Helgeson et al. (1978)	298.15	-35.4	-74.2	-129.75	8.0	
Barany (1962)§	298.15		$-73.9 \pm 4.4$			
Ogorodova et al. (1996)	298.15		$-85.7 \pm 1.9$			

 TABLE 4. Standard thermodynamic properties of analcime hydration

\* Calculated from calorimetric results.

+ Calculated from equilibrium observations.

‡ Retrieved by Bish and Carey (2001) from observations of Balgord and Roy (1973).

§ Calculated from data of Barany (1962) by Johnson et al. (1982).

It should be noted that the values of  $\Delta \overline{H}_{R,T,P}$  measured by immersion calorimetry are somewhat lower than the  $\Delta H_{R,T,P}^{o}$  determined by the equilibrium observations and subsequent regression calculations performed in this study. The cause of this discrepancy is unclear, but is likely related to the difficult nature of the immersion experiments due to the slow hydration kinetics of analcime. Nonetheless, both data sets are generally within error of each other and provide independent assessments of the magnitude of  $\Delta H_{R,T,P}^{o}$ . We prefer the values derived from the equilibrium observations because of the somewhat lower errors associated with the regression calculations and the difficulties inherent in the calorimetric observations.

The only direct observations of  $\Delta S^{\circ}_{R,T_{ref},P_{ref}}$  available for comparison with the results of this study are those obtained by Johnson et al. (1982) through low-temperature adiabatic calorimetry. King (1955) and King and Weller (1961) also measured low-temperature  $C_P^{\circ}$  of analcime and dehydrated analcime, respectively. However, their observations are limited to T > 50 K, precluding model-independent assessment of Third Law entropies from their data (which are generally consistent with those of Johnson et al. 1982). Although similar in magnitude,  $\Delta S^{\circ}_{R,T_{ref},P_{ref}}$  determined by Johnson et al. (1982) is significantly less negative than obtained in this study. As discussed by Neuhoff and Wang (2007b) with regards to  $C_P^{\circ}$  for dehydrated analcime measured by Johnson et al. (1982), this discrepancy likely is not brought about by the minor difference in composition between the samples used in the two studies. Rather, it is probably a result of the procedures employed by these authors in handling the dehydrated analcime sample. It appears from their thorough discussion of experimental methods that the dehydrated analcime sample was re-exposed to laboratory air after dehydration, which likely led to partial rehydration of the sample. Because hydrated analcime has a higher specific heat than dehydrated analcime, molar heat capacities calculated for dehydrated analcime in their study (based on the assumption that their sample was fully dehydrated) are erroneously large, which in turn would lead to an overestimation of the entropy for this phase. Were their sample actually fully dehydrated (or they had been able to accurately account for the true hydration state), the resulting value of  $\Delta S^{\circ}_{R,T_{ref},P_{ref}}$  would be more similar to that obtained in this study.

Although similar in magnitude, our regressed thermodynamic data for analcime hydration are systematically more energetic than those regressed by Bish and Carey (2001) from the phaseequilibrium observations of Balgord and Roy (1973). In part, this discrepancy reflects a difference between the solid-solution model used in this study and in Bish and Carey (2001). In fitting the observations of Balgord and Roy (1973), Bish and Carey (2001) allowed for non-ideal mixing between analcime and dehydrated analcime. This assumption, combined with the lower  $\Delta C_{PR}^{\circ}$  assumed by Bish and Carey (2001;  $\Delta C_{PR}^{\circ} = 8.314$  J/molK at all temperatures), accounts in part for the less-energetic values that they obtained. More significant, perhaps, is the inconsistency between the equilibrium observations of this study with those of Balgord and Roy (1973). Our equilibrium observation data at  $P_{\rm H20}$  of ~0.013 bar are compared with those of Balgord and Roy (1973) obtained by stepwise thermogravimetry at  $P_{\rm H2O}$  of ~0.010 bar in Figure 4. The difference between these two data sets at temperatures above 573 K probably results from the different  $P_{\rm H_{2O}}$  conditions employed. However, as described above, analcime dehydration could not reach equilibrium below 553 K under our experimental conditions. Below this temperature, the data of Balgord and Roy (1973) exhibit progressively lower water contents with decreasing temperature than suggested by our data. Because of this, we believe that the lowest temperature data points of Balgord and Roy (1973) did not achieve equilibrium upon rehydration (similar to the complication encountered in this study) due to kinetic effects and thus pertain to nonequilibrium states of analcime hydration. The net effect of incomplete hydration on the thermodynamic retrievals would be to destabilize analcime relative to dehydrated analcime as shown by the properties calculated by Bish and Carey (2001).

Also shown in Table 4 are the thermodynamic properties of reaction 1 consistent with the data for analcime and dehydrated analcime presented by Helgeson et al. (1978) in their compilation of thermodynamic properties of rock-forming minerals. As discussed below, these values were used by Helgeson et al. (1978) to account for discrepancies between phase-equilibrium observations for univariant reactions involving analcime. The properties used by Helgeson were based on estimated volumetric contributions of water molecules to  $V^{\circ}$  for analcime and the calorimetric observations of King (1955), King and Weller (1961), and Barany (1962). Consistent with the comparisons made above, the use of the data of Barany (1962) led Helgeson et al. (1978) to derive thermodynamic properties suggesting that analcime is considerably less stable relative to dehydrated analcime than found in this study. The implications of this discrepancy are explored below.

# Implications for analcime stability in geological and experimental systems

Partial dehydration of zeolites at elevated temperature is widely recognized as an important factor governing their stability in geologic and engineered systems. For instance, Neuhoff and Bird (2001) demonstrated that the thermal stability of laumontite relative to stilbite and heulandite known from geologic systems and experimental phase equilibria are inconsistent with measured entropies and volumes of these phases if partial dehydration of laumontite is taken into account. Similarly, Carey and Bish (1996) and Wilkin and Barnes (1998) showed that calculated equilibria involving clinoptilolite are significantly affected by dehydration of this phase. To assess the importance of this phenomenon on phase relations involving analcime, the thermodynamic data for reaction 1 reported above were used to evaluate the hydration state of analcime as a function of temperature and pressure in equilibrium with liquid and/or vapor phase water. These calculations were conducted with the aid of the computer code SUPCRT92 (Johnson et al. 1992) and its associated equation of state for  $H_2O$ .

Figure 7 shows isopleths of constant water content of analcime as a function of temperature and pressure consistent with the thermodynamic properties reported in Tables 3 and 4. Note the logarithmic scale for pressure and the liquid vapor saturation curve for water shown for reference. At pressures above the liquid-vapor saturation curve and temperatures below the critical point for  $H_2O$ , analcime is essentially completely hydrated. Below the liquid vapor saturation curve, and at elevated temperatures, dehydration becomes significantly more extensive.

The gray boxes in Figure 7 illustrate geologic and experimental observations that constrain the temperature and pressure conditions of its formation in nature. Most analcime occurrences reported in the literature involve its formation as an authigenic phase in volcanic and immature sedimentary rocks (e.g., Walker 1960; Hay 1966; Iijima 1978; Neuhoff et al. 1997). Figure 7 shows observations of in situ T-P conditions attending analcime formation in nature: formation in saline, alkaline lakes at the surface of the Earth (box a; e.g., Hay 1986), formation by hydrothermal alteration of basaltic lavas in Icelandic geothermal systems (box b; Smárason et al. 1989), and diagenesis of silicic vitric tuffs in Japan (box c; Iijima 1978). Comparison between the isopleths of analcime hydration state and the T-P conditions denoted by boxes a, b, and c in Figure 7 indicates that analcime is essentially fully hydrated in these environments. This same observation holds true even for higher-temperature parageneses involving analcime. Box d in Figure 7 shows the estimated conditions of formation of analcime in the Ilímaussaq intrusive complex in South Greenland based on geological evidence and fluid inclusion studies of coexisting tugtupite (Sobolev et al. 1970; Markl 2001). Even though the T-P conditions estimated for these occurrences likely represent the maximum thermal conditions associated with the analcime-albite-tugtupite parageneses, the distribution of analcime isopleths relative to these conditions in Figure 7 still suggest that it is essentially fully hydrated.

The occurrence of analcime as a phenocryst phase in some alkaline lavas has been the subject of a vigorous debate, with some workers arguing for a primary, igneous paragenesis for these occurrences and others arguing that analcime is a secondary replacement of another phenocryst phase, most likely leucite (e.g., Knight 1904; Daly 1912; Washington 1914; Mackenzie 1915; Prisson 1915; Larsen and Buie 1938; Wilkinson 1968, 1977; Pearce 1970; Gupta and Fyfe 1975; Taylor and Mackenzie 1975; Church 1978, 1979; Luhr and Kyser 1989; Karlsson and Clayton 1991; Pearce 1993). In large part, this debate is centered



**FIGURE 7.** Hydration state of analcime as a function of temperature and pressure (corresponding to total  $H_2O$  pressure) calculated from the thermodynamic properties listed in Tables 3 and 4. The bold curve represents the liquid-vapor saturation curve for water (solid circle is the critical point). The gray areas depict geologic and experimental observations of the temperature and pressure conditions of analcime formation in nature: (**a**) saline alkaline lakes (Hay 1986); (**b**) Icelandic geothermal systems (Smárason et al. 1989); (**c**) Japanese sediments (Iijima 1978); (**d**) South Greenland syenites (Markl 2001); and (**e**) alkaline magmas (Peters et al. 1966; Kim and Burley 1971; Roux and Hamilton 1976). The dashed arrows depict the eruption and cooling history of analcime-phyric lavas (see text). The empty circles and solid arrow depict the evolution of temperature during heating of analcime at 1 bar vapor pressure in a radioactive waste repository (see text).

around the need for such a magma to contain sufficient H<sub>2</sub>O to form analcime, and thus the hydration state of analcime under liquidus conditions is an important part of the debate. Experimental equilibrium phase relations in the system nepheline (NaAlSiO<sub>4</sub>)kalsilite (KAlSiO<sub>4</sub>)-silica (SiO<sub>2</sub>)-H<sub>2</sub>O have demonstrated that analcime can coexist with a melt in a narrow range of pressure (5-13 kb) and temperature (600-640 °C) conditions (e.g., Peters et al. 1966; Kim and Burley 1971; Roux and Hamilton 1976). This range of conditions is denoted by box e in Figure 7. It can be seen that if analcime does form as a liquidus phase under these conditions, it is nearly fully hydrated provided sufficient H<sub>2</sub>O is available. The dashed arrows in Figure 7 represent a simplified eruption and cooling path experienced by such lavas. Eruption of the lavas would lead to a significant loss of water (up to  $\sim 94\%$ ). Subsequent cooling of the lavas at low pressure would then lead to rehydration of analcime. Although analcime would experience rather drastic changes in hydration state along such a T-P path, it is unlikely to have much textural effect since the volume change upon dehydration is minimal (Table 4).

Analcime is also potentially an important phase in many radioactive waste repository settings. Reaction of alkaline solutions from Portland cement porewaters with bentonite-based barriers that is a likely consequence of many repository designs has been shown through geochemical modeling and laboratory studies to lead to analcime formation (e.g., Chermak 1992; Savage and Rochelle 1993; Savage et al. 2001). Although not widespread in the repository zone at Yucca Mountain, analcime does occur at greater depths in Yucca Mountain, Nevada (Bish et al. 2003) and potentially may form during heating of the repository from clinoptilolite and mordenite that are the main authigenic zeolites in the repository zone (e.g., Carey and Bish 1996; Bish et al. 2003; Bish and Aronson 1993). Emplacement of high-level radioactive waste will affect the long-term behavior of zeolites at Yucca Mountain and other repositories due to the heat produced by the radioactive decay of the waste. The solid arrow in Figure 7 represents the thermal evolution of analcime as temperature increases from 298 to 523 K at a constant pressure of 33 mbar. The dehydration behavior of analcime under these conditions, as well as under various other humidity conditions (corresponding to  $P_{\rm H_{20}}$  of 1, 0.015, and 0.005 bar) are shown in Figure 8a. It can be seen in Figure 8a that the hydration state of analcime in waterundersaturated conditions is very sensitive to both temperature and vapor pressure. In the case of the thermal evolution depicted in Figure 7, our model predicts that analcime will lose ~24.5%  $H_2O$  at 0.33 bar. At 523 K, this value varies from ~1% at  $P_{H_2O}$  = 1 bar to almost 70% at  $P_{\rm H_{2O}} = 0.005$  bar.

These results can be further used to evaluate the thermal consequences of dehydration of analcime. Figure 8b shows the cumulative heat necessary to raise the temperature of analcime from 298.15 K to elevated repository temperatures (at 1 bar total pressure) based on the compositions shown in Figure 8a and the variation of  $\Delta H^{\circ}_{R,T,P}$  with temperature calculated from the data in Tables 3 and 4. The lowermost curve in Figure 8b represents the heat necessary to raise the temperature of analcime without taking dehydration into account (i.e., only considering  $C_P^{\circ}$  of analcime). The other curves include both the consequences of heating analcime and the thermal effects of partial dehydration. It can be seen that dehydration significantly increases the amount of heat necessary to raise the temperature of analcime; for example, ~37% more heat is necessary to raise the temperature of analcime to 523 K at  $P_{\rm H_{2O}} = 0.033$  bar if dehydration is taken into account. Given the magnitudes of the heat effects involved, the dehydration of analcime could be an important consideration in evaluating thermal budgets in systems where this mineral is abundant.

Experimental observations of phase relations involving analcime at elevated temperatures and pressures have proven notoriously difficult to reconcile with each other (Thompson 1973; Helgeson et al. 1978; Neuhoff et al. 2004). This is particularly true of univariant phase equilibria involving analcime, such as those reported for the reactions (using the nominal "ideal" stoichiometry of analcime):

$$NaAlSi_2O_6 \cdot H_2O + SiO_2 = NaAlSi_3O_8 + H_2O,$$
(9)  
analcime quartz albite

$$2 \text{ NaAlSi}_{2}\text{O}_{6} \cdot \text{H}_{2}\text{O} = \text{NaAlSi}_{3}\text{O}_{8} + \text{NaAlSiO}_{4} + \text{H}_{2}\text{O}, \quad (10)$$
  
analcime albite nepheline

and

$$NaAlSi_2O_6 \cdot H_2O = NaAlSi_2O_6 + H_2O$$
(11)  
analcime jadeite

reported by Greenwood (1961), Campbell and Fyfe (1965), Liou (1971), Thompson (1971), Kim and Burley (1971), and Manghnani (1970). Thompson (1973) attributed these difficulties to errors in tabulated thermodynamic properties for analcime and

**FIGURE 8. (a)** Analcime hydration state as a function of *T* and  $P_{\rm H_{2O}}$  calculated using the thermodynamic properties in Tables 2 and 3. (b) Cumulative heat necessary to raise the temperature of analcime from 298.15 K to elevated *T*. Dashed curve corresponds to enthalpy necessary to heat analcime without dehydration. Solid curves correspond to enthalpy necessary to heat and dehydrate analcime to the extents depicted in panel **a** at different  $P_{\rm H_{2O}}$ .

albite and to solid solution in analcime (particularly with respect to the NaAlO<sub>2</sub>-SiO<sub>2</sub> $\cdot$ 0.5H<sub>2</sub>O substitution present in this phase. Helgeson et al. (1978) invoked variable degrees of solid solution in experimental run products to resolve inconsistencies between experimental and calculated Clapeyron slopes for reaction 9 as well, but attributed the apparent inconsistency between reported equilibria for reactions 9 and 10 to the effects of partial dehydration of analcime under the conditions of reaction 10.

Figure 9 shows isopleths of analcime hydration state calculated using the thermodynamic properties of this study (solid curves) along with those calculated using the data and equations of Helgeson et al. (1978; dashed curves). The boxes in Figure 9 show the positions of experimental reversals for reactions 9, 10, and 11 considered by Thompson (1973) and Helgeson et al. (1978). It can be seen in Figure 9 that the thermodynamic properties determined in this study indicate considerably lower degrees of dehydration of analcime at elevated T-P than do those of Helgeson et al. (1978). This is a consequence of the thermodynamic data available at the time of the study of Helgeson et al. (1978), which were based largely on the value of  $\Delta H^{\circ}_{R,T_{\text{ref}},P_{\text{ref}}}$  from the study of Barany (1962), which appears to be incorrect (see above). In addition, Helgeson et al. (1978) estimated the value of  $\Delta V_{\rm R}^{\circ}$  to be 8 cm<sup>3</sup>/mol based on the volumetric differences and water contents of laumontite, "leonhardite" (partially dehydrated





**FIGURE 9.** Calculated hydration state of analcime using the thermodynamic properties of the present study (dashed curves) and those reported by Helgeson et al. (1978; dotted curves). Solid curve is the liquid-vapor saturation curve for water. Shown for comparison are experimental reversals of univariant phase equilibria corresponding to reactions 9 (white boxes), 10 (gray boxes), and 11 (black boxes) reported by Greenwood (1961), Campbell and Fyfe (1965), Liou (1971), Thompson (1971), Kim and Burley (1971), and Manghnani (1970).

laumontite), and wairakite. As discussed above, more recent unit-cell observations on homologous hydrated and dehydrated analcimes suggests that this property is considerably smaller (Table 4). The much large values of  $\Delta V_{R}^{o}$  adopted by Helgeson et al. (1978) led to considerably more shallow Clapeyron slopes than those calculated in this study.

Although both Helgeson et al. (1978) and the present study predict that analcime is essentially fully hydrated under the conditions of reaction 9, predictions by Helgeson et al. (1978) suggest considerably larger degrees of dehydration of analcime attending reactions 10 and 11. The calculations made using the data of the present study indicate that analcime is essentially fully hydrated at the conditions of almost all of the experimental brackets in Figure 9 (the minimum water content corresponding to  $X_{hydrated analcime}$  of ~0.97). In contrast, the predictions made by Helgeson et al. (1978) indicate that the reversals reported for reaction 10 correspond to  $X_{hvdrated analcime}$  of ~0.90, which allowed them to reconcile the results for reactions 9 and 10. Given that the thermodynamic properties of reaction 1 determined in this study do not predict substantial dehydration of analcime under the conditions of reaction 10, we feel that the apparent difference between the reversals reported for reactions 9 and 10 is not a consequence of diminished activity of analcime due to the dehydration. Rather, as suggested by Thompson (1973), the more likely cause of the discrepancy is that analcime coexisting with albite and nepheline under the conditions of reaction 10 is probably silica deficient relative to that in equilibrium with albite, quartz, and water per reaction 9.

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#### **REFERENCES CITED**

Apps, J.A. (1970) The stability field of analcime, 347 p. Ph.D. thesis, Harvard University, Cambridge.

- Baldar, N.A. and Whittig, L.D. (1968) Occurrence and synthesis of soil zeolites. Soil Science Society of America Proceedings, 32, 235–238.
- Balgord, W.D. and Roy, R. (1973) Crystal chemical relationships in the analcite family. II. Influence of temperature and P<sub>H20</sub> on structure. Molecular Sieves, 16, 189–199.
- Barany, R. (1962) Heats and free energies of formation of some hydrated and anhydrous sodium- and calcium-aluminum silicates: U.S. Bureau of Mines Report of Investigations 5900, 17 p.
- Bish, D.L. and Aronson, J.L. (1993) Paleogeothermal and paleohydrologic conditions in silicic tuff from Yucca Mountain, Nevada. Clays and Clay Minerals, 41, 148–161.
- Bish, D.L. and Carey, J.W. (2001) Thermal behavior of natural zeolites. In D.L. Bish and D.W. Ming, Eds., Natural Zeolites: Occurrences, Properties, Applications, 45, p. 403–452. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.
- Bish, D.L., Vaniman, D.T., Chipera, S.J., and Carey, J.W. (2003) The distribution of zeolites and their effects on the performance of a nuclear waste repository at Yucca Mountain, Nevada, U.S.A. American Mineralogist, 88, 1889–1902.
- Bockheim, J.G. and Ballard T.M. (1975) Hydrothermal soils of the crater of Mt. Baker, Washington. Soil Science Society of America Proceedings, 39, 997–1001.
- Boles, J.R. (1991) Diagenesis during folding and uplift of the Southland Syncline, New Zealand. New Zealand Journal of Geology and Geophysics, 34, 253–259.
- Cammenga, H.K., Eysel, W., Gmelin, E., Hemminger, W., Höhne, G.W.H., and Sarge, S.M. (1993) The temperature calibration of scanning calorimeters 2. Calibration Substances. Thermochimica Acta, 219, 333–342.
- Campbell, A.S. and Fyfe, W.S. (1965) Analcime-albite equilibria. American Journal of Science, 263, 807–816.
- Carey, J.W. and Bish, D.L. (1996) Equilibrium in the clinoptilolite-H<sub>2</sub>O system. American Mineralogist, 81, 952–962.
- Chermak, J.A. (1992) Low temperature experimental investigation of the effect of high pH NaOH solutions on the Opalinus Shale, Switzerland. Clays and Clay Minerals, 40, 650–658.
- Chipera, S.J. and Bish, D.L. (1991) Rehydration behavior of natural analcime, p. 29. Clay Minerals Society, 28th Annual Meeting, Houston, Texas.
- Church, B.N. (1978) Shackanite and related analcite-bearing lavas in British Columbia. Canadian Journal of Earth Sciences, 15, 1669 1672.
- ——(1979) Shackanite and related analcite-bearing lavas in British Columbia: Reply. Canadian Journal of Earth Sciences, 16, 1229–1302.
- Coombs, D.S. (1954) The nature and alteration of some Triassic sediments from Southland, New Zealand. Transactions of the Royal Society of New Zealand, 82, 65–109.
- Cooper, J.R. (1982) Representation of the ideal-gas thermodynamic properties of water. International Journal of Thermophysics, 3, 35–43
- Cruciani, G. and Gualtieri, A. (1999) Dehydration dynamics of analcime by in situ synchrotron powder diffraction. American Mineralogist, 84, 112–119.
- Daly, R.A. (1912) The geology of the North American Cordillera at the forty-ninth parallel. Geological Survey of Canada Memoir, 38, P857.
- de'Gennaro, M., Petrosino, P., Conte, M.T., Munno, R., and Colella, C. (1990) Zeolite chemistry and distribution in a Neapolitan yellow tuff deposit. European Journal of Mineralogy, 2, 779–786.
- Gmelin, E. and Sarge, S.M. (2000) Temperature, heat and heat flow rate calibration of differential scanning calorimeters. Thermochimica Acta, 347, 9–13.
- Gottardi, G., and Galli, E. (1985) Natural zeolites, 409 p. Springer Verlag, Berlin.
- Greenwood, H.J. (1961) The system NaAlSi<sub>2</sub>O<sub>6</sub>-H<sub>2</sub>O-argon: Total pressure and water pressure in metamorphism. Journal of Geophysical Research, 66, 3923–3946.
- Gupta, A.K. and Fyfe, W.S. (1975) Leucite survival: The alteration to analcime. Canadian Mineralogist, 13, 361–363.
- Hay, R.L. (1966) Zeolites and zeolitic reactions in sedimentary rocks. Geological Society of America Special Paper, 85, 130 p.
- —— (1978) Geologic occurrence of zeolites. In L.B. Sand and F.A. Mumpton, Eds., Natural Zeolites: Occurrence, Properties, Use, p. 135–143. Pergamon Press, New York.
- ——(1986) Geologic occurrence of zeolites and some associated minerals. Pure and Applied Chemistry, 58, 1339–1342.
- Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A, 229 p.
- Höhne, G.W.H., Cammenga, H.K., Eysel, W., Gmelin, E., and Hemminger, W. (1990) The temperature calibration of scanning calorimeters. Thermochimica Acta, 160, 1–12.
- Iijima, A. (1978) Geological occurrences of zeolite in marine environments. In L.B. Sand and F.A. Mumpton, Eds., Natural Zeolites: Occurrence, Properties, and Applications, p. 175–198. Pergamon Press, New York.
- (1988) Diagenetic transformations of minerals as exemplified by zeolites and silica minerals; a Japanese view. In G.V. Chilingarian, Ed., Diagenesis II,

Developments in Sedimentology, 43, p. 147-209. Elsevier, Amsterdam.

- Johnson, G.K., Flotow, H.E., O'Hare, P.A.G., and Wise, W.S. (1982) Thermodynamic studies of zeolites: Analcime and dehydrated analcime. American Mineralogist, 67, 736–748.
- Johnson, J.W., Oelkers, E.H., and Helgeson, H.C. (1992) SUPCRT92: Software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions among them as functions of temperature and pressure. Computers in Geoscience, 18, 899–947.
- Karlsson, H.R. and Clayton, R.N. (1991) Analcime phenocrysts in igneous rocks: Primary or secondary? American Mineralogist, 76, 189–199.
- Kim, K.T. and Burley, B.J. (1971) Phase equilibria in the system NaAlSi<sub>3</sub>O<sub>8</sub>-NaAl-SiO<sub>4</sub>-H<sub>2</sub>O with special emphasis on the stability of analcite. Canadian Journal of Earth Sciences, 8, 311–337.
- King, E.G. (1955) Low temperature heat capacity and entropy at 298.16 K of analcite. Journal of the American Chemical Society, 77, 2192–2193.
- King, E.G. and Weller, W.W. (1961) Low-temperature heat capacities and entropies at 298.15 K of some sodium- and calcium-aluminum silicates. U.S. Bureau of Mines Report of Investigations 5855, 1–8.
- Knight, C.W. (1904) Analcite-trachyte tuffs and breccias from south-west Alberta, Canada. Canadian Record of Science, 9, 265–278.
- Larsen, E.S. and Buie, B.F. (1938) Potash analcime and pseudoleucite from the Highwood Mountains of Montana. American Mineralogist, 23, 837–849.
- Liou, J.G. (1971) P-T stabilities of laumontite, wairakite, lawsonite, and related minerals in the system CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. Journal of Petrology, 12, 379–411.
- Luhr, J.F. and Kyser, T.K. (1989) Primary igneous analcime: The Colima minettes. American Mineralogist, 74, 216–223.
- Mackenzie, J.D. (1915) The primary analcime of the Crowsnest volcanics. American Journal of Science, 39, 571–574.
- Maier, C.G. and Kelley, K.K. (1932) An equation for the representation of high temperature heat content data. American Chemical Society Journal, 54, 3243–3246.
- Manghnani, M.H. (1970) Analcite-jadeite phase boundary. Physics of the Earth and Planetary Interiors, 3, 456–461.
- Markl, G. (2001) A new type of silicate liquid immiscibility in peralkaline nepheline syenites (lujavrites) of the Ilimaussaq complex, South Greenland. Contributions to Mineralogy and Petrology, 241, 458–472.
- Mazzi, F. and Galli, E. (1978) Is each analcime different? American Mineralogist, 63, 448–460.
- Murphy, W.M., Pabalan, R.T., Prikryl, J.D., and Goulet, C.J. (1996) Reaction kinetics and thermodynamics of aqueous dissolution and growth of analcime and Na-clinoptilolite at 25 °C. American Journal of Science, 296, 128–186.
- Neuhoff, P.S. and Bird, D.K. (2001) Partial dehydration of laumontite: Thermodynamic constraints and petrogenetic implications. Mineralogical Magazine, 65, 59–70.
- Neuhoff, P.S. and Wang, J. (2007a) Isothermal measurement of heats of hydration in zeolites by simultaneous thermogravimetry and differential scanning calorimetry. Clays and Clay Minerals, 55, 239–252.
- (2007b) Heat capacity of hydration in zeolites. American Mineralogist, 92, 1358–1367.
- Neuhoff, P.S., Watt, W.S., Bird, D.K., and Pedersen, A.K. (1997) Timing and structural relations of regional zeolite zones in basalts of the East Greenland continental margin. Geology, 25, 803–806.
- Neuhoff, P.S., Stebbins, J.F., and Bird, D.K. (2003) Si-Al disorder and solid solutions in analcime, chabazite, and wairakite. American Mineralogist, 88, 410–423.
- Neuhoff, P.S., Hovis, G.L., Balassone, G., and Stebbins, J.F. (2004) Thermodynamic properties of analcime solid solutions. American Journal of Science, 304, 21–66.
- Newton, M.S. and Kennedy, G.C. (1968) Jadeite, analcite, nepheline and albite at high temperatures and pressures. American Journal of Science, 266, 728–735.
- Ogorodova, L.P., Kiseleva, I.A., Melchakova, L.V., Belitskii, I.A., and Fursenko, B.A. (1996) Enthalpies of formation and dehydration of natural analcime. Geokhimiya, 1088–1093.
- Pearce, T.H. (1970) The analcite-bearing volcanic rocks of the Crowsnest Formation, Alberta. Canadian Journal of Earth Sciences, 7, 46–66.
- —— (1993) Analcime phenocrysts in igneous rocks: Primary or secondary?— Discussion. American Mineralogist, 78, 225–229.
- Peters, T., Luth, W.C., and Tuttle, D.F. (1966) The melting of analcime solid solutions in the system NaAlSiO<sub>4</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O. American Mineralogist, 51, 736–753.
- Prisson, L.V. (1915) The Crowsnest volcanics. American Journal of Science, 39, 222–223.
- Putnis, A., Giampaolo, G., and Graeme-Barber, A. (1993) High temperature X-ray diffraction and thermogravimetric analysis of the dehydration of analcime, NaAlSi<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O. EUG VII, Strasbourg 1993, Terra Abstracts, 5, 497 p.
- Redkin, A.F. and Hemley, J.J. (2000) Experimental Cs and Sr sorption on analcime in rock-buffered systems at 250–300 °C and P<sub>sat</sub> and the thermodynamic

evaluation of mineral solubilities and phase relations. European Journal of Mineralogy, 12, 999–1014.

- Renaut, R.W. (1993) Zeolitic diagenesis of llate Quaternary fluviolacustrine sediments and associated calcrete formation in the Lake Bogoria Basin, Kenya Rift Valley. Sedimentology, 40, 271–301.
- Roux, J. and Hamilton, D.L. (1976) Primary igneous analcite-an experimental study. Journal of Petrology, 17, 244–257.
- Sabbah, R., An, X.W., Chickos, J.S., Leitao, M.L.P., Roux, M.V., and Torres, L.A. (1999) Reference materials for calorimetry and differential thermal analysis. Thermochimica Acta, 331, 93–204.
- Sarge, S.M., Gmelin, E., Hohne, G.W.H., Cammenga, H.K., Hemminger, W., and Eysel, W. (1994) The caloric calibration of scanning calorimeters. Thermochimica Acta, 247, 129–168.
- Savage, D. and Rochelle, C. (1993) Modeling reactions between cement pore fluids and rock: implications for porosity change. Journal of Contaminant Hydrology, 13, 365–378.
- Savage, D., Rochelle, C., Moore, Y., Milodowski, A., Bateman, K., Bailey, D., and Mihara, M. (2001) Analcime reactions at 25–90 °C in hyperalkaline fluids. Mineralogical Magazine, 65, 571–587.
- Sheppard, R.A. and Hay, R.L. (2001) Formation of zeolites in open hydrologic systems. In D.L. Bish and D.W. Ming, Eds., Natural Zeolites: Occurrence, Properties, Applications, 45, p. 261–275. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.
- Smárason, O.B., Tómasson, J., and Ganda, S. (1989) Alteration mineralogy of the Elliðaár geothermal field, Reykjavík, Iceland. In D.L. Miles, Ed., Water-Rock Interaction, 6, p. 643–646. Taylor and Francis, London.
- Sobelev, V.S., Bazarova, T.Y., Shugarova, N.A., Bazarov, L.Sh., Dolgov, Tu.A., and Sørensen, H. (1970) A preliminary examination of fluid inclusions in nepheline, sorensite, tugtupite, and chaklovite from the Ilímaussaq alkaline intrusion, South Greenland. Bulletin of the Grønlands Geologiske Undersøgelse, 81, 32 p.
- Stølen, S., Glöckner, R., and Grønvold, F. (1996) Heat capacity of the reference material synthetic sapphire (α-Al<sub>2</sub>O<sub>3</sub>) at temperatures from 298.15 to 1000 K by adiabatic calorimetry. Increased accuracy and precision through improved instrumentation and computer control. Journal of Chemical Thermodynamics, 28, 1263–1281.
- Taylor, D. and Mackenzie, W.S. (1975) A contribution to the pseudo-leucite problem. Contributions to Mineralogy and Petrology, 49, 321–333
- Thompson, A.B. (1971) Analcite-albite equilibria at low temperatures. American Journal of Science, 271, 79–92.
- —— (1973) Analcime: Free energy from hydrothermal data. Implications for phase equilibria and thermodynamic quantities for phase in NaAlO<sub>2</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. American Mineralogist, 58, 277–286.
- Utada, M. (1965) Zonal distribution of authigenic zeolites in the Tertiary pyroclastic rocks in Mogami district, Yamagata Prefecture. Tokyo University College General Education Science, 15, 173–216.
- van Reeuwijk, L.P. (1974) The Thermal Dehydration of Natural Zeolites, 88 p. H. Veenman and Zonen B.V., Wageningen, The Netherlands.
- Walker, G.P.L. (1960) Zeolite zones and dike distribution in relation to the structure of the basalts of eastern Iceland. Journal of Geology, 68, 515–528.
- Washington, H.S. (1914) The analcite basalts of Sardinia, Journal of Geology, 22, 743–753.
- Wilkin, R.T. and Barnes, H.L. (1998) Solubility and stability of zeolites in aqueous solution: I. Analcime, Na-, and K-clinoptilolite. American Mineralogist, 83, 746–761.
- Wilkinson, J.F.G. (1968) Analcimes from some potassic igneous rocks and aspects of analcime-rich igneous assemblages. Contributions to Mineralogy and Petrology, 18, 252–269.
- (1977) Analcime phenocrysts in a vitrophyric analcimite—primary or secondary? Contributions to Mineralogy and Petrology, 64, 1–10.
- Wilkinson, J.F.G. and Hensel, H.D. (1994) Nephelines and analcimes in some alkaline igneous rocks. Contributions to Mineralogy and Petrology, 118, 79–91.
- Wilkinson, J.F.G. and Whetten, J.T. (1964) Some analcime-bearing pyroclastic and sedimentary rocks from New South Wales. Journal of Sedimentary Petrology, 34, 543–553.
- Wise, W.S. (1984) Thermodynamic studies of zeolites: Analcime solid solutions. In D. Olson and A. Bisio, Eds., Proceedings of the Sixth International Zeolite Conference, p. 616–623. Guildford, Butterworths, U.K.
- Woolley, A.R. and Symes, R.F. (1976) The analcime-phyric phonolites (blairmorites) and associated analcime kenytes of the Lupata Gorge Mozambique. Lithos, 9, 9–15.z

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