Chabazite: Energetics of hydration, enthalpy of formation, and effect of cations on stability

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ABSTRACT

The stability of synthetic cation-exchanged zeolites having the chabazite framework (CHA) and their cation-water interaction were studied using high-temperature reaction calorimetry. Four cations (K, Na, Li, and Ca) were exchanged into CHA. The enthalpies of formation were determined for all samples, and the partial molar enthalpy of hydration was measured by varying the water content of one Ca-CHA.

The enthalpy of formation depends strongly on the exchanged cation, becoming more exothermic in the order Ca, Li, Na, K. The integral hydration enthalpy does not depend strongly on the nature of the cation, but becomes slightly less exothermic with increasing aluminum content. For the one Ca-CHA studied in detail, the average enthalpy of hydration is -34.6 ± 1.2 kJ/mol relative to liquid water. A quadratic fit to the transposed temperature drop data gives $\Delta \bar{h}_{H_2O} = -52.97 \ (\pm 4.74) + 2.94 \ (\pm 0.68) \ n$ (kJ/mol), where $\Delta \bar{h}_{H_2O}$ is the partial molar enthalpy of hydration and n is the number of water molecules per 24 oxygen formula.

INTRODUCTION

Zeolites $[(Li,Na,K)_a(Mg,Ca,Sr,Ba)_d(Al_{(a+2d)}Si_{n-(a+2d)}O_{2n}) \cdot m H_2O]$ are hydrated framework aluminosilicates that incorporate molecular H_2O in structural pores. The interaction of water with cations and with the framework in a zeolite cage is important in a variety of applications, including pollution abatement, catalysis, cation exchange, and gas separation. Thermodynamic data are essential to evaluate zeolite stability and characterize the hydration process. Zeolite minerals occur in several near-surface geologic settings. Thermodynamic data help determine their paragenesis.

Extra-framework cations and the Al/Si ratio affect stability and hydration of zeolites. Barrer and Langley (1958) and Barrer and Baynham (1956) found that the thermal stability (temperature at which the zeolite decomposes on heating at a constant rate) of chabazite increased in the order Li, Na, K, Rb, Cs, and water retentivity increased in the order Rb, K, Na, Li. Cartlidge and Meier (1984) observed that Na-exchanged natural chabazite showed solid-state transformation to a sodalite structure at 600 °C in a dry nitrogen atmosphere, whereas K-exchanged natural chabazite did not transform. According to their Rietveld refinement, Na and K occupied different positions and coordination states with H_2O molecules and framework O atoms.

Although these observations are mostly qualitative and both kinetic and thermodynamic factors are probably involved, it is obvious that the cations play an important role in zeolite stability.

Many studies have shown that there are two major types of water in the zeolite cage: one has strong interaction and may be associated with the hydration of the extra-framework cations, and the other has little interaction with the zeolite and may simply fill the voids. For example, leonhardite ($CaAl_2Si_4O_{12} \cdot 3.5H_2O$) shows significant differences in the enthalpy of hydration associated with H_2O molecules in different positions (Kiseleva et al. 1996a). Although the loss of one mole of H_2O in the initial stage of dehydration has a near zero enthalpy of interaction (6.4 ± 9.2 kJ/mol, relative to liquid water), removal of the water molecules from the Ca coordination sphere requires 40.2 ± 2 kJ/mol. Carey and Bish (1996, 1997) studied the clinoptilolite-H_2O equilibrium and measured the partial molar enthalpies of hydration. The hydration enthalpies became less exothermic in the sequence Ca, Na, K at low water content, but converged to similar values at saturation.

Water having weak interaction with the framework was also observed in cordierite, $Mg_2Al_4Si_5O_{18} \cdot nH_2O$. Cordierite absorbs water on a well-defined crystallographic site without hydration of any cations. Its enthalpy of hydration (relative to liquid H_2O) is zero over a range of water contents (Carey and Navrotsky 1992). This implies that the molecular environment of H_2O in cordierite is energetically similar to that of H_2O in liquid water.

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Hydration may be a complex process of H_2O gain and structural rearrangement coupled with extra-framework cation movement (chabazite: Smith 1962; Smith and Rinaldi 1963; Mortier et al. 1977; zeolite Y: Dooryhee et al. 1991; heulandite: Armbruster and Gunter 1991). Although some structural studies proposed the sites for extra-framework cations and H_2O molecules (Alberti et al. 1982), the numbers and locations of such sites are often difficult to deduce even from single-crystal X-ray structure refinements because of ambiguity in site assignments, positional disorder of H_2O, and difficulty in accounting for the effects of different cations (Carey and Bish 1996).

Vieillard (1995) proposed a method of predicting enthalpy of formation based on known crystal structures and applied it to zeolites. However, ambiguity in the determination of cation sites and H_2O location in zeolite cages hinders the accurate prediction of energetics using such models. Therefore, to understand better the cation-water interaction in zeolite cages, it is necessary to determine accurate energetic data for the hydration process as well as structural variation during hydration. Such an understanding is essential to predicting the energetics, mechanisms, and rates of hydration and dehydration of zeolites in natural environments ranging from soils to volcanic glass. A better understanding of the influence of the cation on the stability of a zeolite is desirable to allow design of catalysts and adsorbents with the high thermal stability required to survive activation in commercial processes. By choosing appropriate mixtures of cations, adsorbents with good performance and improved thermal stability can be developed.

This study focuses on chabazite (ideal form Ca_2Al_4 $Si_8O_{24} \cdot 12H_2O$) and reports heats of formation and heats of hydration for several synthetic materials having the CHA-framework type. The enthalpies of formation for the cation-exchanged chabazites were measured using high-temperature, drop-solution calorimetry in molten lead borate to investigate the effect of cation type and Al/Si ratio on energetics. To observe the hydration energetics in detail, transposed-temperature, drop calorimetry was performed for one Ca-CHA sample with varying water content. For all other samples, an integral enthalpy of hydration, obtained from transposed-temperature, drop calorimetry, is reported.

EXPERIMENTAL METHODS

Synthesis and characterization of initial chabazite samples

All the chabazite (CHA) samples were synthesized in the potassium form, using different methodologies depending on the Si/Al ratio desired. At the highest Si/Al ratio, the K-CHA was prepared via a zeolite to zeolite conversion similar to that of Bourgogne (1985). A 2 M KOH solution was prepared. To 300 cc of that caustic solution, 142.22 g of a colloidal silica solution (Nalco 2326, which is an ammonia-stabilized, colloidal silica solution, nominally 14.5 wt% SiO_2) was added. This mixture was also clear and colorless. Fifty grams of a commercial hydrogen zeolite (HY) powder (LZY-62 analyzed by the manufacturer as 72.2 wt% SiO_2, 24.0 wt% Al_2O_3, 2.55 wt% Na_2O) was added and the mixture was briefly homogenized by shaking the container. The sealed container was placed in a forced-air oven set at 100 °C. After 5 days, the solid was separated from the clear solution using vacuum filtration, and the

solid product was washed with deionized water while on the filter. The solid was allowed to air dry on the filter and was recovered. X-ray powder diffraction (XRD) showed a pattern typical for a K-CHA with an Si/Al ratio above 2.5. ^{29}Si NMR determined the framework Si/Al ratio to be 2.65, in good agreement with the elemental analysis (Si/Al = 2.7, Na/Al = 0.02, K/Al = 1.07). The other K-CHA samples were prepared using standard gel synthesis techniques (Barrer et al. 1959). To prepare CHA samples with Si/Al $\cong$ 1.5 some $Sr(NO_3)_2$ was used in the synthesis. These samples retain Sr after ion exchange. Chemical analyses of all zeolite samples were done by inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AA).

Ion exchange and characterization

Cation-exchanged chabazite samples were prepared by Air Products and Chemicals, Inc. For example, the Ca ion-exchanged form of CHA 084-32 was prepared using batch ion exchange, by contacting the K-CHA with a 2 M solution of $CaCl_2$ at a solution to solid ratio of 25 cc/g. The mixture was heated overnight at 100 °C, washed with deionized water, and air dried on the filter prior to the next exchange. A total of five exchanges were conducted. This was necessary to overcome the unfavorable exchange of K out of the zeolite. Elemental analysis revealed an excess of Ca (Ca/Al = 1.06 on an equivalent fraction basis) in the solid. This excess suggests the possibility of imbibed salt into the chabazite, as is often the case with unfavorable ion-exchange isotherms, however, no chloride was detected. In addition, ~4% of the original K ions remained after this exchange procedure. Other ion-exchanged forms were prepared using similar standard batch techniques with excesses of the exchanging cations.

Thermal analysis to determine H_2O content was done on a TGA 2951, TA Instruments, using an N_2 purge and a 10 °C/min ramp rate. Analytical data are summarized in Table 1.

Throughout this paper, we use the term hydrated or "fully hydrated" to mean samples having water contents representative of their initial preparation followed by equilibration for several weeks in our laboratory (23 ± 1 °C and 50 ± 5% relative humidity).

Preparation of partially hydrated samples

To investigate the energetics of hydration in more detail, we selected a sample (084-32) that does not change its structure during transposed-temperature drop calorimetry (TTD) to 700 °C. This was confirmed by measuring the powder XRD patterns using a Scintag PAD-V diffractometer before and after heating for one hour at 700 °C. The pattern of the heated samples showed only minor changes, namely, peak shifts to higher angle, likely due to water loss (see Fig. 1). To determine the water content of the sample, thermogravimetric analysis was performed on a Netzsch Thermal Analyzer STA 409 in static air using a pellet weighing about 40 mg. The water content of the initial sample was 22.27 wt%.

Because dehydrated Ca-CHA hydrates spontaneously under ambient conditions, its hydration rate was determined to control the water content. The sample was completely hydrated overnight and then heated at 700 °C for 1 hour. The mass

TABLE 1. Chemical compositions of CHA-zeolites (moles per 24-oxygen formula)

Major cation	Sample	Si	Al	Ca	Li	Na	K	Mg	Zn	Sr	H$_2$O
Ca	113-91	8.66	3.34	1.58	0.00	0.00	0.36	0.00	0.00	0.00	12.83
	084-32	8.77	3.23	1.63	0.00	0.03	0.13	0.00	0.00	0.00	12.54
	084-99	7.09	4.91	2.24	0.00	0.00	0.52	0.00	0.00	0.00	14.68
	084-11	7.93	4.07	2.29	0.00	0.04	0.04	0.00	0.00	0.00	13.40
	084-48	7.20	4.80	2.80	0.00	0.00	0.06	0.00	0.00	0.08	12.95
	084-84	7.29	4.71	2.84	0.00	0.00	0.08	0.00	0.00	0.00	15.16
Li	084-51	8.75	3.25	0.00	3.05	0.13	0.01	0.00	0.00	0.00	11.79
	113-92	8.68	3.32	0.00	3.17	0.15	0.01	0.00	0.00	0.00	10.88
	084-34	7.11	4.89	0.00	3.75	0.15	0.02	0.00	0.00	0.17	12.52
	084-27	8.04	3.96	0.00	3.27	0.62	0.02	0.00	0.00	0.00	12.59
	084-60	7.96	4.04	0.00	3.76	0.20	0.01	0.00	0.00	0.00	12.70
	084-96	7.04	4.96	0.00	4.70	0.24	0.01	0.00	0.00	0.00	14.52
	084-87	6.25	5.75	0.00	5.60	0.02	0.00	0.00	0.00	0.00	15.17
Na	113-90	8.69	3.31	0.00	0.00	3.33	0.01	0.00	0.00	0.00	11.69
	084-53	8.00	4.00	0.00	0.00	3.95	0.01	0.00	0.00	0.00	12.57
	084-16	8.02	3.98	0.00	0.00	4.28	0.02	0.00	0.00	0.00	11.89
	084-95	7.14	4.86	0.02	0.00	4.40	0.01	0.00	0.02	0.00	13.36
	084-85	6.15	5.85	0.02	0.00	5.51	0.01	0.00	0.00	0.00	16.50
K	113-89	8.69	3.31	0.00	0.00	0.00	3.23	0.00	0.00	0.00	8.90
	084-14	8.82	3.18	0.00	0.00	0.00	3.39	0.00	0.00	0.00	9.88
	084-93	7.11	4.89	0.00	0.00	0.00	4.79	0.00	0.00	0.00	10.63
	084-77	6.13	5.87	0.08	0.00	0.00	5.39	0.00	0.00	0.00	10.71
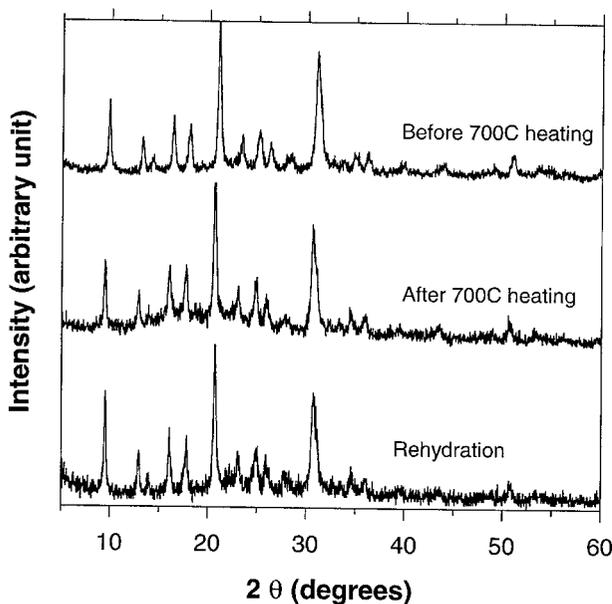
FIGURE 1. The X-ray diffraction (XRD) patterns of Ca-CHA (084-32). Top pattern is for original sample, middle pattern for sample heated one hour at 700 °C, bottom for rehydrated sample.

changes were measured under ambient conditions and in a glove box. In ambient air, the sample was completely hydrated in 20 minutes. The atmosphere in the glove box is Ar purified using a 5 Å molecular sieve to have a moisture content of <50 ppm. To determine the hydration state of the zeolite maintained in the glove box, the sample was immediately placed into the glove box after heating and its mass change was measured. The water content changed by ~5 wt% during 70 hours. After observation in the glove box, the mass change under ambient conditions was also measured for the same sample. The sample was completely hydrated under 12 hours. This indicates that CHA is a very efficient getter for traces of H$_2$O in the glove box.

These rate studies enabled the selection of conditions for preparation of partially hydrated samples. After being completely hydrated under ambient conditions overnight, portions of the sample were heated at various temperatures between 300 and 700 °C for 1 hour and then immediately placed in the glove box. Pellets of 10–20 mg were made in the glove box. The water contents were measured by mass change, assuming that the completely hydrated sample contained 22.27 wt% of water as determined by TGA. Each water content was confirmed by measuring the mass change of a portion of each sample after complete hydration under ambient conditions. All samples, except the ones with 5–7 wt% H$_2$O, were completely rehydrated under ambient conditions. The hydration experiments confirmed within error the water content measured by dehydration. The samples that contained 5–7 wt% H$_2$O were hydrated to 15–17 wt% H$_2$O in ambient condition, as confirmed by TGA. The XRD patterns of all samples confirm retention of the CHA framework (Fig. 1).

Calorimetry

The enthalpies of formation and hydration were determined using a Tian-Calvet high-temperature, heat-flux microcalorimeter (Navrotsky 1997). All experiments were done under 40 cm^3/min flow of Ar gas. For drop-solution calorimetry, the samples were dropped from room temperature into molten 2PbO·B$_2$O$_3$ at 700 °C. The heat of drop solution was a sum of the heat of solution in the melt plus the heat content. The water was totally evolved into the atmosphere of the calorimeter at 700 °C and did not interact with the solvent (Navrotsky et al. 1994). Heats of dehydration were studied using TTD calorimetry, in which the sample was dropped into an empty Pt crucible in the calorimeter. The heat effect contained two contributions, the enthalpy of dehydration at 700 °C and the heat content of the sample. All calorimetric experiments were performed using pressed pellets about 3 mm in diameter, 1–2 mm in height, and 10–20 mg in weight.

The calorimeter was calibrated using pressed pellets of powdered corundum (α-Al$_2$O$_3$) of weight similar to that of the

TABLE 2. Calorimetric data for ion-exchanged CHA-zeolites*

Major cation	Sample	ΔH_{TTD} (J/g)	(kJ/mol)	ΔH_{DS} (J/g)	(kJ/mol)	ΔH_{SOL} (kJ/mol)
Ca	113-91	1716.7 ± 21.1	1761.1 ± 21.6	1573.4 ± 21.1	1614.1 ± 21.6	−147.0 ± 30.6
	084-32	1789.0 ± 12.5	1814.8 ± 12.7	1627.7 ± 5.4	1651.2 ± 5.5	−163.6 ± 13.8
	084-99	1753.8 ± 18.9	1911.9 ± 20.6	1704.8 ± 11.0	1858.5 ± 12.0	−53.4 ± 23.8
	084-11	1779.4 ± 13.1	1872.3 ± 13.8	1671.8 ± 9.2	1759.1 ± 9.7	−113.2 ± 16.8
	084-48	1701.2 ± 9.1	1821.3 ± 9.7	1670.9 ± 9.8	1788.9 ± 10.5	−32.4 ± 14.3
	084-84	1798.9 ± 6.0	1989.3 ± 6.6	1770.4 ± 6.5	1947.9 ± 7.2	−31.5 ± 9.8
Ca	084-32 partially hydrated					
	(1.044 ± 0.234)‖	810.1 ± 9.5	654.0 ± 7.3			
	(2.635 ± 0.046)‖	995.2 ± 22.0	832.0 ± 18.2			
	(3.177 ± 0.037)‖	1073.2 ± 36.5	907.7 ± 30.9			
	(4.975 ± 0.040)‖	1250.9 ± 17.1	1098.5 ± 14.7			
	(7.655 ± 0.007)‖	1479.3 ± 32.5	1370.5 ± 30.0			
	(9.294 ± 0.081)‖	1613.8 ± 20.0	1542.8 ± 20.2			
	(11.677 ± 0.300)‖	1751.6 ± 22.5	1749.9 ± 31.5			
	(12.540 ± 0.02)‖	1789.0 ± 12.5	1814.8 ± 12.7			
Li	084-51	1748.0 ± 4.7	1668.2 ± 4.5	1754.0 ± 7.5	1674.0 ± 7.2	5.7 ± 8.4
	113-92	1698.7 ± 15.0	1595.4 ± 14.1	1704.2 ± 23.1	1600.6 ± 21.7	5.2 ± 25.9
	084-34	1833.1 ± 8.9	1808.0 ± 8.8	1900.8 ± 17.6	1874.8 ± 17.4	66.8 ± 19.5
	084-27	1799.1 ± 11.1	1765.2 ± 10.9	1886.9 ± 16.8	1851.4 ± 16.5	86.2 ± 19.8
	084-60	1808.3 ± 20.0	1765.7 ± 19.5	1868.3 ± 17.3	1824.2 ± 16.9	58.5 ± 25.8
	084-96	1823.4 ± 21.3	1851.9 ± 21.6	1893.4 ± 15.3	1923.5 ± 15.5	71.6 ± 26.6
	084-87	2003.5 ± 9.5	2058.2 ± 9.8	2068.1 ± 4.9	2124.5 ± 5.0	66.3 ± 11.0
Na	113-90	1649.1 ± 20.1	1657.2 ± 20.2	1643.9 ± 26.0	1652.0 ± 26.1	−5.2 ± 33.0
	084-53	1648.4 ± 16.7	1704.9 ± 17.3	1778.7 ± 15.7	1839.6 ± 16.2	134.8 ± 23.7
	084-16	1666.8 ± 4.8	1716.9 ± 4.9	1787.9 ± 10.1	1841.5 ± 10.4	124.7 ± 11.5
	084-95	1652.4 ± 12.9	1750.9 ± 13.8	1801.9 ± 14.7	1909.3 ± 15.6	158.4 ± 20.7
	084-85	1709.0 ± 10.3	1947.7 ± 11.7	1876.4 ± 3.8	2138.5 ± 4.3	190.8 ± 12.5
K	113-89	1402.6 ± 11.1	1408.2 ± 11.1	1526.8 ± 19.6	1532.9 ± 19.7	124.7 ± 22.6
	084-14	1433.3 ± 11.2	1473.5 ± 11.5	1561.6 ± 8.7	1605.4 ± 8.9	131.9 ± 14.6
	084-93	1428.1 ± 7.9	1562.9 ± 8.6	1619.3 ± 14.6	1772.2 ± 16.0	209.2 ± 18.2
	084-77	1430.6 ± 8.5	1599.7 ± 9.5	1677.3 ± 6.2	1875.5 ± 6.9	275.8 ± 11.8

* Molar value is for 24 O atoms (12 TO$_2$) formula unit. Uncertainty is two standard deviations of the mean. TTD = transposed temperature drop, DS = drop solution, SOL = solution (see text).
‖ Water content, n = number of moles H$_2$O per 24 O atoms.

sample (Kiseleva et al. 1996a). The corundum (Johnson Matthey 99.999%) was heated at 1500 °C for 15 h to ensure dryness, crystallinity, and complete conversion to α–Al$_2$O$_3$. The calibration factors for the calorimeters were confirmed by TTD calorimetry of monoclinic ZrO$_2$ (baddeleyite), which reproduced its known heat content.

Calorimetric results

The enthalpies of drop solution (ΔH_{DS}) and of TTD (ΔH_{TTD}) of the fully hydrated zeolites are given in Table 2. The enthalpy of solution at 700 °C of the dehydrated framework is the difference between the enthalpy of drop solution and of transposed temperature drop, $\Delta H_{SOL} = \Delta H_{DS} - \Delta H_{TTD}$. The transposed temperature drop data, ΔH_{TTD}, for the partially hydrated Ca-CHA sample are also given in Table 2.

The enthalpies of formation can be calculated directly from ΔH_{DS} using thermodynamic cycles. An example of such a calculation is shown as cycle A in Appendix 1. The calculated enthalpies of formation from the oxides and from the elements at 25 °C are given in Table 3, together with a summary of chemical formulas. Other high-temperature, oxide-melt solution calorimetric data needed for this calculation are listed in Table 4.

The enthalpy of formation of the anhydrous CHA-framework at different Al/(Al+Si) and different cation content can be calculated (see Table 3) relative to the oxides at 700 °C from the heats of solution and the subsidiary thermochemical data given in Table 4. A sample calculation is given as cycle B in Appendix 1.

DISCUSSION

Enthalpies of formation

The enthalpies of formation from the oxides of the fully hydrated zeolites are shown as a function of aluminum content, N_{Al} {$N_{Al} = 12[Al/(Al+Si)]$}, in Figure 2. For all cations, the enthalpy of formation becomes more negative with increasing Al content, with the trends being roughly linear for each zeolite series. For a given Al content, the enthalpy of formation becomes more negative in the sequence Ca, Li, Na, K. This trend of increasing energetic stability with increasing oxide basicity or decreasing ionic potential (z/r) is commonly seen in ternary oxides and silicates (Navrotsky 1994). An analogous trend was observed in the DTA and XRD study of Barrer and Langley (1958), although DTA studies are influenced by the rate of decomposition (kinetic factors) as well as by energetics (thermodynamic factors). The enthalpies of formation calculated by Vieillard (1995) are similar for Ca (within ~10–20 kJ/mol) but significantly less exothermic (by ~150 kJ/mol) for Na than the measured data.

The observed trends must be interpreted with some caution for two reasons. First, each zeolite has a different water content (n ranges from 8.9 to 15.2, although most of the samples have n between 12.5 and 13.5). Thus, differences in hydration energetics may cause variations of ~10 kJ/mol (see magnitudes of hydration enthalpies discussed below) in the enthalpies of formation from the oxides. Indeed, it is interesting that most samples have more than the "ideal" H$_2$O content of n = 12.

Table 3. Thermodynamic data for ion exchanged CHA-zeolites

Major cation	Sample	Formula	Cation charge	Frame work charge	A	B	C	D
Ca	113-91	$(Ca_{1.58}K_{0.36})(Si_{8.66}Al_{3.34})O_{24}\cdot12.83\ H_2O$	3.52	−3.34	−271.4 ± 21.9	−15692.1 ± 23.7	−25.6	37.0 ± 147.0
	084-32	$(Ca_{1.63}K_{0.13}Na_{0.03})(Si_{8.77}Al_{3.23})O_{24}\cdot12.54\ H_2O$	3.42	−3.23	−310.5 ± 6.4	−15652.6 ± 11.2	−32.7	76.2 ± 163.6
	084-99	$(Ca_{2.24}K_{0.52})(Si_{7.09}Al_{4.91})O_{24}\cdot14.68\ H_2O$	5.00	−4.91	−391.8 ± 12.5	−16675.1 ± 15.0	−22.6	−78.6 ± 53.6
	084-11	$(Ca_{2.29}Na_{0.04}K_{0.04})(Si_{7.93}Al_{4.07})O_{24}\cdot13.40\ H_2O$	4.66	−4.07	−349.9 ± 10.3	−16281.5 ± 13.5	−21.0	20.4 ± 113.3
	084-48	$(Ca_{2.80}K_{0.06}Sr_{0.08})(Si_{7.20}Al_{4.80})O_{24}\cdot12.95\ H_2O$	5.82	−4.80	−413.3 ± 11.2	−16529.6 ± 13.9	−26.9	−70.5 ± 32.7
	084-84	$(Ca_{2.84}K_{0.08})(Si_{7.29}Al_{4.71})O_{24}\cdot15.16\ H_2O$	5.76	−4.71	−428.9 ± 8.1	−17165.1 ± 11.7	−25.2	−78.0 ± 31.7
Li	084-51	$(Li_{3.05}Na_{0.13}K_{0.01})(Si_{8.75}Al_{3.25})O_{24}\cdot11.79\ H_2O$	3.19	−3.25	−378.2 ± 7.9	−15380.0 ± 12.5	−24.8	−106.1 ± 6.3
	113-92	$(Li_{3.17}Na_{0.15}K_{0.01})(Si_{8.68}Al_{3.32})O_{24}\cdot10.88\ H_2O$	3.33	−3.32	−368.9 ± 22.0	−15145.5 ± 24.0	−24.3	−109.9 ± 5.8
	084-34	$(Li_{3.75}Na_{0.15}K_{0.02})(Si_{7.11}Al_{4.89})O_{24}\cdot12.52\ H_2O$	4.26	−4.89	−522.7 ± 17.8	−15929.4 ± 19.8	−26.3	−160.0 ± 66.9
	084-27	$(Li_{3.27}Na_{0.62}K_{0.02})(Si_{8.04}Al_{3.96})O_{24}\cdot12.59\ H_2O$	3.91	−3.96	−520.5 ± 16.9	−15868.4 ± 19.2	−24.0	−222.5 ± 86.3
	084-60	$(Li_{3.76}Na_{0.20}K_{0.01})(Si_{7.96}Al_{4.04})O_{24}\cdot12.70\ H_2O$	3.97	−4.04	−464.3 ± 17.3	−15895.4 ± 19.6	−23.1	−172.7 ± 58.6
	084-96	$(Li_{4.70}Na_{0.24}K_{0.11})(Si_{7.04}Al_{4.96})O_{24}\cdot14.52\ H_2O$	4.95	−4.96	−435.1 ± 16.0	−16608.7 ± 18.5	−16.2	−202.1 ± 71.7
	084-87	$(Li_{5.60}Na_{0.02})(Si_{6.25}Al_{5.75})O_{24}\cdot15.17\ H_2O$	5.62	−5.75	−574.3 ± 6.7	−17097.7 ± 11.6	−24.8	−190.9 ± 66.4
Na	113-90	$(Na_{3.33}K_{0.01})(Si_{8.69}Al_{3.31})O_{24}\cdot11.69\ H_2O$	3.34	−3.31	−515.1 ± 26.3	−15235.8 ± 27.9	−23.1	−263.2 ± 5.9
	084-53	$(Na_{3.95}K_{0.01})(Si_{8.00}Al_{4.00})O_{24}\cdot12.57\ H_2O$	3.96	−4.00	−666.8 ± 16.6	−15717.4 ± 18.7	−19.3	−441.8 ± 134.8
	084-16	$(Na_{4.28}K_{0.02})(Si_{8.02}Al_{3.98})O_{24}\cdot11.89\ H_2O$	4.30	−3.98	−735.6 ± 11.0	−15663.5 ± 13.9	−24.6	−461.7 ± 124.7
	084-95	$(Na_{4.40}K_{0.01}Zn_{0.02})(Si_{7.14}Al_{4.86})O_{24}\cdot13.36\ H_2O$	4.48	−4.86	−693.1 ± 16.0	−16018.1 ± 17.9	−18.0	−485.7 ± 158.4
	084-85	$(Na_{5.51}K_{0.01}Ca_{0.02})(Si_{6.15}Al_{5.85})O_{24}\cdot16.50\ H_2O$	5.56	−5.85	−755.2 ± 6.0	−17130.4 ± 9.6	−10.6	−593.6 ± 190.8
K	113-89	$(K_{3.23})(Si_{8.69}Al_{3.31})O_{24}\cdot8.90\ H_2O$	3.23	−3.31	−712.4 ± 20.0	−14529.8 ± 22.2	−24.2	−529.0 ± 124.7
	084-14	$(K_{3.39})(Si_{8.82}Al_{3.18})O_{24}\cdot9.88\ H_2O$	3.39	−3.18	−734.7 ± 9.6	−14871.5 ± 13.7	−25.6	−559.9 ± 131.9
	084-93	$(K_{4.79})(Si_{7.11}Al_{4.89})O_{24}\cdot10.63\ H_2O$	4.78	−4.89	−959.7 ± 16.5	−15439.8 ± 19.0	−32.7	−784.2 ± 209.3
	084-77	$(K_{5.39})(Si_{6.13}Al_{5.87})O_{24}\cdot10.71\ H_2O$	5.39	−5.87	−1101.1 ± 8.3	−15641.7 ± 12.4	−22.6	−908.7 ± 275.9

Notes: A = Enthalpy of formation of hydrated CHA from oxides at 25 °C (kJ/mol). B = Enthalpy of formation of hydrated CHA from elements at 25 °C (kJ/mol). C = Enthalpy of hydration, kJ per mole of liquid H_2O, calculated by cycle C in Appendix 1. Calculation uses estimated heat content of dehydrated zeolite obtained from correlation discussed in Appendix 2. Uncertainty is about ± 4 kJ/mol when one considers all sources of error in data and approximations used. D = Enthalpy of formation of dehydrated CHA from oxides at 700 °C (kJ/mol).

Second (see Table 3), the extra-framework cation charge does not exactly balance the framework charge arising from Al. The formulas in Table 1 and Table 3 are balanced in terms of oxide stoichiometry and refer to 12 tetrahedral units (24 oxygen atoms) but the analytical data suggest significant excess Ca in the Ca-CHA samples. Some of the Li, Na, and K samples are slightly cation-rich, others slightly cation-poor, and others stoichiometric. The variations for Li, Na, and K are probably within experimental error, but the Ca-excess appears real. Chemical analysis shows that very little Cl⁻ or other anions are present,

so the excess Ca must be charged-balanced by oxide or hydroxide ions. If the excess CaO is present as $Ca(OH)_2$, with the hydration of CaO coming from the water content of the sample, then one can rewrite the formula of the sample as a mixture of idealized zeolite and excess portlandite. For example, sample 084-32, $(Ca_{1.63}K_{0.13}Na_{0.03})(Si_{8.77}Al_{3.23})O_{24}\cdot12.54\ H_2O$ would be $(Ca_{1.54}K_{0.13}Na_{0.03})(Si_{8.77}Al_{3.23})\ O_{24}\cdot12.36\ H_2O + 0.09Ca(OH)_2$. Correcting for this excess $Ca(OH)_2$ as a separate phase would make the enthalpies of formation of the Ca-CHA zeolites less exothermic by 5–15 kJ/mol, depending on the amount of ex-

Table 4. Calorimetric data for oxides used in thermochemical cycles

	ΔH_{DS} (kJ/mol)	ΔH_{SOL} (kJ/mol)
SiO_2 (quartz)	39.1 ± 0.3*	−4.3 ± 0.2*
Al_2O_3 (α)	107.9 ± 1.0*	33.0 ± 0.8*
CaO	−17.6 ± 0.7†	−51.2 ± 1.0†
Li_2O	−18.4 ± 0.7‡	−68.2 ± 1.0‡
Na_2O	−113.1 ± 0.8§	−170.8 ± 0.9§
K_2O	−193.7 ± 1.1§	−261.0 ± 1.2§
MgO	36.5 ± 1.0‖	4.8 ± 1.0‖
SrO	−58.5 ± 2.2#	−93.6 ± 2.0#
ZnO	38.1 ± 1.0**	4.9 ± 10.6**
H_2O	69.1 ± 1.2††	–

* Kiseleva et al. (1996a).
† Calculated from Kiseleva et al. (1996a) and heat of formation of $CaCO_3$ and heat content of CaO (Robie et al. 1978).
‡ Xu et al. (submitted 1999) and calculated using heat content of Li_2O in Robie et al. (1978).
§ Kiseleva et al. (1996b).
‖ Smelik et al. (1994).
\# Bularzik et al. (1991).
** Davies and Navrotsky (1981).
†† Heat content of H_2O [liquid reference state at 25 °C, Robie et al. (1978)].
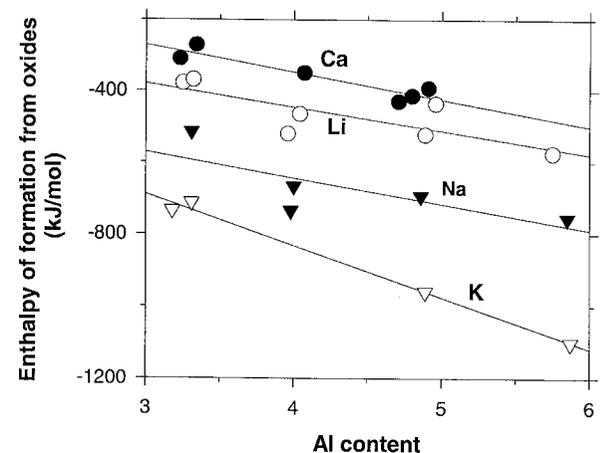
FIGURE 2. The enthalpy of formation for cation exchanged hydrated CHA from binary oxides at 25 °C vs. total Al content. The estimated 2σ uncertainty lies within the size of the symbol. The lines are least-squares fits.

cess calcium. However if the Ca is in the channels [imbibed $Ca(OH)_2$ or some other species], this may interact energetically with the zeolite, making the correction to the enthalpy uncertain. It is even possible that the "ideal stoichiometric" Ca-CHA never exists and that these Ca-rich compositions are stable relative to the idealized structure. Such compositional complexity in both synthetic and natural zeolites is ubiquitous and there is no unique way of dealing with it. The scatter seen in thermodynamic trends in this study may reflect the variability in cation and water content, but the overall trends are valid and useful. Given the inherent ambiguity in making compositional corrections to the data to calculate thermodynamic parameters for idealized compositions, we have chosen to present the data as measured, with heats of formation calculated for compositions obtained by chemical analysis. Though this choice is somewhat arbitrary, it probably best reflects the chemical composition of the samples actually being dissolved in the calorimetric experiments.

It is also worth noting that the formula units (and molecular weights) used for these zeolites are large. They are chosen to be consistent with the crystallographic data (unit-cell size) but may also be considered fairly arbitrary. The resulting enthalpies of formation are very large in magnitude with correspondingly large errors. Yet the uncertainty (±10–20 kJ/mol) in the heat of formation from the oxides (–300 to –1000 kJ/mol) is 2–5%. The uncertainty in the measured enthalpies of transposed temperature drop and drop solution is on the order of ±1%.

Petrova (1997) reported the enthalpy of formation of several zeolites, including a Ca-rich natural chabazite having the composition (converted to a 24 oxygen basis) $(Ca_{1.64}Mg_{0.02}Na_{0.44}K_{0.16})(Al_{3.6}Si_{8.14}Fe_{0.02})O_{24} \cdot 12.45\ H_2O$, by oxide melt drop solution calorimetry. Its enthalpy of formation from the oxides (24 oxygen basis) was reported to be -617.0 ± 13.8 kJ/mol. This value is substantially more exothermic than our

values for Ca-CHA samples with similar Si/Al ratios, –300 to –350 kJ/mol. However, Petrova (1997) gave few experimental details. She used a value for the enthalpy of solution of H_2O in lead borate of –28 kJ/mol. Such a value may be appropriate under static atmosphere where some water remains dissolved (Navrotsky et al. 1994), but such experiments can lead to uncertain final states. In contrast, calorimetry under a flowing atmosphere, where all H_2O is expelled (and has a zero enthalpy of interaction with the solvent), has been shown to be a much better calorimetric procedure (Navrotsky et al. 1994). If one assumes that all water was in fact expelled from the solvent in the experiments of Petrova, then the enthalpy of formation from the oxides would be more positive by $12.46 \times 28 = 349$ kJ. This would give an enthalpy of formation from the oxides of –268 kJ/mol, somewhat more positive than our values. Thus ambiguity in the final state of water could have a very large effect on measured enthalpies of formation of H_2O-rich materials. We stress that in our experiments under flowing gas, the final state of water is well understood (Navrotsky et al. 1994; Kiseleva et al. 1996a).

The enthalpies of solution (Fig. 3) of the dehydrated zeolites at 700 °C from the oxides show similar trends with Al content and with cation as those shown by hydrated samples, namely, increasing stability with increasing Al/(Al+Si) and with increasing cation basicity. Here some additional caution is warranted. Whereas the Ca-CHA samples maintained a crystalline zeolitic framework on dehydration, the alkali chabazites showed considerable loss of peak intensity and a "glassy hump" in their XRD patterns, indicating significant amorphization. Thus the "dehydrated CHA" may often be partly, and in some cases, mostly, amorphous. However, the effect of this amorphization on the overall energetics is likely to be quite small (generally <10 kJ/mol and often <5 kJ/mol) for several reasons. Several other anhydrous zeolite frameworks have enthalpies within 3–5 kJ/mol (on a two oxygen basis) of glass of the same composition: SiO_2 (Petrovic et al. 1993); faujasite (Petrovic and Navrotsky 1997); leonhardite (Kiseleva et al. 1996a); and analcime (Robie and Hemingway 1995). Thus, especially for a zeolite of intermediate framework density such as chabazite, the enthalpy of complete vitrification is fairly small (probably <20 kJ/mol on a 12 TO_2 basis). The dehydrated zeolites produced in this study are generally not completely amorphous and may retain some additional short-range order, making the energetic effect of amorphization even smaller. Furthermore, the observed heats of solution (see Fig. 3) do not show any obvious irregularities although the degree of crystallinity varies for different cations and for different Al-contents for the same cation. Thus the energetics of dehydrated zeolites reported here are probably meaningful estimates for the CHA-framework.

Natural chabazites occur with values of N_{Al} of about 3.5 to 4.5 (Al/(Al+Si) = 0.29 to 0.38) (Gottardi and Galli 1985). This same range is covered in the synthetic CHA-zeolites studied here, so the data obtained in this study on synthetic materials should be directly applicable to natural chabazites. Natural chabazites, like many other natural zeolites, tend to have Ca as the primary charge-balancing cation, probably reflecting the chemistry of the aqueous solutions from which they form. This places them in the range of relatively less negative heats of formation among
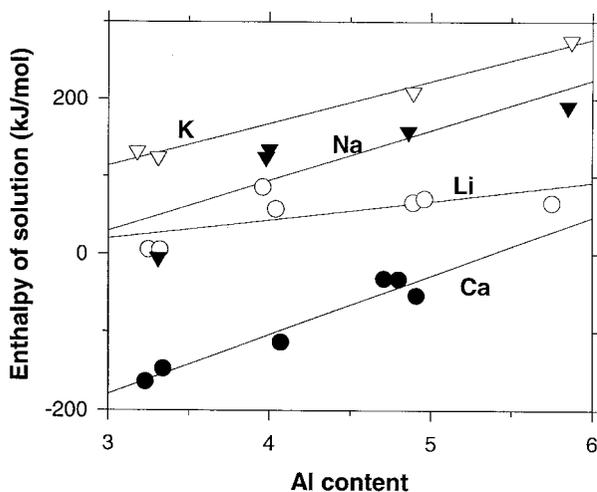

FIGURE 3. The enthalpy of solution in $2PbO \cdot B_2O_3$ at 700 °C for cation exchanged dehydrated CHA vs. Al content. The lines are least-squares fits.

the systems studied. However, the hydrated zeolite would be energetically stable with respect to the corresponding dense aluminosilicates plus water, and would have a stability field at low temperature. For example, for sample 084-32, including excess Ca, a possible decomposition reaction can be written as

$$(Ca_{1.63}K_{0.13}Na_{0.03})(Si_{8.77}Al_{3.23})O_{24} \cdot 12.54 \ H_2O(CHA) = 0.13KAlSi_3O_8 \text{ (microcline)} + 0.03NaAlSi_3O_8 \text{ (albite)} + 1.54CaAl_2Si_2O_8 \text{ (anorthite)} + 0.09CaSiO_3\text{(wollastonite)} + 5.12SiO_2 \text{ (quartz)} + 12.54 \ H_2O \text{ (water)} \quad (1)$$
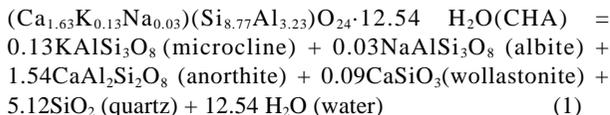
For this reaction, $\Delta H = 113.6 \pm 15.0$ kJ/mol at 25 °C (liquid water reference state), using our calorimetric data plus data from Robie and Hemingway (1995).

The entropy change for this decomposition reaction would be positive, becoming strongly positive at pressures and temperatures where the water is gaseous. This balance of positive ΔH and positive ΔS of decomposition limits zeolite stability to low temperature.

In contrast, dehydrated CHA is energetically metastable with respect to its dense oxide mineral components. Thus for dehydrated sample 084-32, the decomposition reaction would be

$$(Ca_{1.54}K_{0.13}Na_{0.03})(Si_{8.77}Al_{3.23})O_{24}(CHA) = 0.13KAlSi_3O_8 \text{ (microcline)} + 0.03NaAlSi_3O_8 \text{ (albite)} + 1.54CaAl_2Si_2O_8 \text{ (anorthite)} + 0.09CaSiO_3\text{(wollastonite)} + 5.12SiO_2 \text{ (quartz)} \quad (2)$$
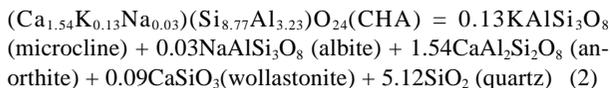
for which $\Delta H_2 = -185.8 \pm 25.0$ kJ/mol. This exothermic enthalpy indicates that the dehydrated CHA is metastable with respect to the dense anhydrous mineral assemblage under all conditions. Per tetrahedral unit (per TO_2), this metastability is 15.6 ± 2.1 kJ/mol. Similar small positive enthalpies (5–15 kJ/mol) relative to dense assemblages have been noted for a series

of zeolitic silica polymorphs (Petrovic et al. 1993), sodium faujasites (Petrovic and Navrotsky 1997), metaleonhardite (Kiseleva et al. 1996a), dehydrated mordenite (Johnson et al. 1992), and dehydrated analcime (Johnson et al. 1982). Thus chabazites, like many other zeolites, owe their stability to hydration, and their dehydrated frameworks are metastable.

Enthalpies of hydration of fully hydrated ion exchanged chabazites

The enthalpy of hydration for the fully hydrated zeolite

$$CHA \ (25 °C) + nH_2O \ (liquid, 25 °C) = CHA \cdot nH_2O \ (25 °C) \quad (3)$$
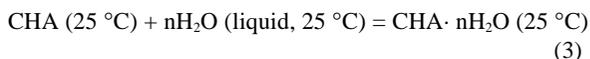
can be calculated from the transposed temperature drop calorimetric data using cycle C shown in Appendix 1. The heat content of the anhydrous zeolite has been estimated to do this calculation (see Appendix 2).

The enthalpies of hydration are given in Table 3 and compared to values for other zeolites in Table 5. The enthalpies of hydration (relative to liquid water) are generally between –20 and –35 kJ per mole of water, even for different zeolite structures.

Figure 4 shows the average enthalpies of hydration of CHA (per mole of water) as a function of Al content. The data show considerable scatter, possibly related to variable water content, excess Ca, and the approximations used in the heat-content calculation for the dehydrated framework (see Appendix 2). There is no strong dependence of the integral enthalpy of hydration on the nature of the cation, although the Ca-samples may show slightly more exothermic values than the alkali (Li, Na, K) samples. The average enthalpy of hydration may become slightly less exothermic with increasing Al content. There is no obvious dependence on the total amount of water (9 < n < 16).
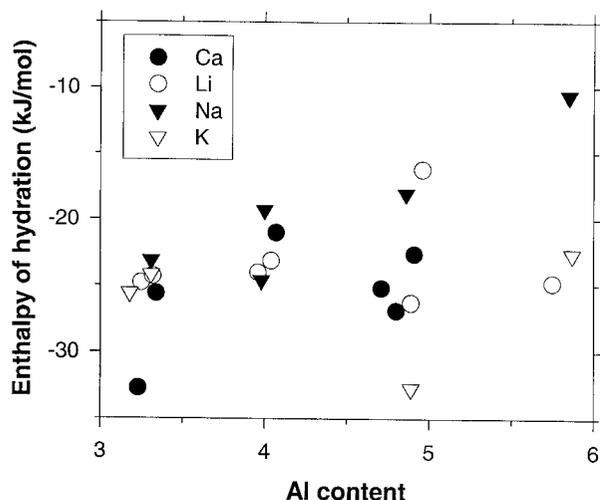

FIGURE 4. The average enthalpy of hydration (kJ per mole of liquid water) vs. Al content for ion exchanged CHA samples.

TABLE 5. Enthalpy of hydration of various zeolites*

Structure	Cation			
	Ca	Li	Na	K
Chabazite	(– 21 to –34)‡	(–16 to –26)‡	(–10 to –25)‡	(–22 to –32)‡
	–33.1 ± 1.2†			
	–37.0##			
Leonhardite	–40.0 ± 2§			–30 ± 3‖
Clinoptilolite	–32.9 ± 2.9#		–30.2 ± 3 .5#	–23.8 ± 1.3#
	–30.3 ± 2.0**		–23.4 ± 0.6**	– 22.4 ± 0.8**
			–22.1††	
			–23.4‡‡	
Analcime			–40.9§§	
Mordenite	–30.0‖			

* Value in kJ per mole of H_2O represents an average enthalpy of hydration normalized to the number of moles of water, liquid water reference state.
† This work, sample 084-32.
‡ Range of values for samples with different Al-contents, this work.
§ Kiseleva et al. (1996a).
‖ Kiseleva et al. (1996b).
Carey and Bish (1996) equilibria.
** Carey and Bish (1997) calorimetry.
†† Barrer and Cram (1971).
‡‡ Johnson et al. (1991).
§§ Johnson et al. (1982).
‖ ‖ Johnson et al. (1992).
Valueva and Goryainov (1992) calorimetry.

Enthalpies of hydration of Ca-chabazite as a function of water content

Figure 5 shows the enthalpies of transposed temperature drop as a function of H_2O content for sample 084-32. A linear regression of all the data results in (ΔH_{TTD} in kJ/mol):

$$\Delta H_{TTD} = 573.9 \ (\pm 8.8) + 102.1 \ (\pm 1.2) \ n, \ r = 0.997 \quad (4)$$

The slope of Equation 4 defines a constant average enthalpy of hydration (relative to liquid H_2O) of -33.0 ± 1.2 kJ/mol, from $n = 0.5$ to $n = 12.5$.

Although the fit of the data to a straight line is excellent, the individual average enthalpy of transposed temperature drop at each water content has a relatively large uncertainty (± 10–30 kJ/mol). This large error is due mainly to the large molecular weight (and correspondingly large molar enthalpy) of the zeolite.

One must ask whether these data warrant fitting to more than one compositional parameter, as would be the case if the partial molar enthalpy of hydration, $\Delta \bar{h}_{H_2O}$, depends on the degree of hydration. Such behavior is generally expected in zeolites, with the first water molecules entering a dehydrated structure more tightly held than those near saturation. We first address this question by calculating values of $\Delta \bar{h}_{H_2O}$ by using the following equation

$$\Delta \bar{h}_{H_2O} = \frac{d\Delta H_{hydration}}{dn} \ \frac{\Delta(\Delta H_{hydration})}{\Delta n} \quad (5)$$

This method does not force $\Delta \bar{h}_{H_2O}$ to any specific functional form. Independent values of $\Delta \bar{h}_{H_2O}$ are calculated for small composition intervals to reveal the functional dependence of $\Delta \bar{h}_{H_2O}$ on n.
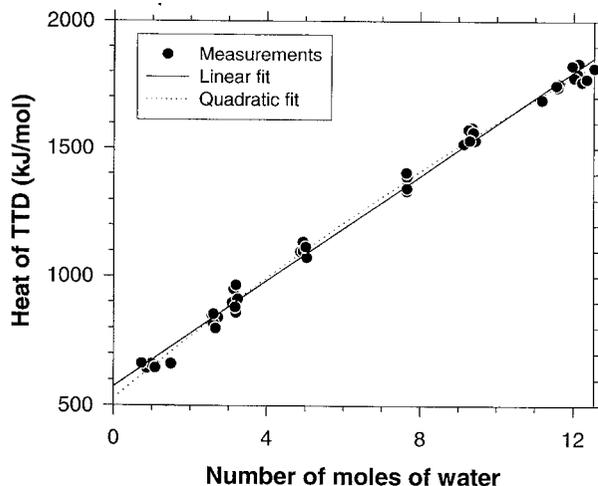
FIGURE 5. The enthalpy of transposed temperature drop for hydrated and partially hydrated Ca-CHA (084-32) as a function of H_2O content. Solid line is a linear fit, whereas the dashed curve is a quadratic fit (see text for equations).

Cycle D in Appendix 1 computes the partial molar enthalpy of H_2O at the average water content, $\bar{n} = (n_1 + n_2)/2$ by using the reaction, at 25 °C

$$CHA \cdot n_1 H_2O + (n_2 - n_1) \ H_2O = CHA \cdot n_2 H_2O \quad (6)$$
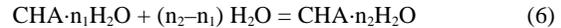
with $\Delta \bar{h}_{H_2O} = \Delta H_6/(n_2 - n_1)$. If n_1 and n_2 are chosen to be too close together, the propagated uncertainty is magnified and resolution is lost. If n_1 and n_2 are too far apart, only an average $\Delta \bar{h}_{H_2O}$, similar to the value obtained from the linear fit to all the data, is obtained. We have chosen to use alternate pairs of data points (giving $n_2 - n_1$ values of 3–5) as the best compromise of error vs. compositional resolution (see Table 6). This approach shows that the partial molar enthalpy of hydration becomes somewhat more exothermic with decreasing water content, ranging from values of -20 ± 10 kJ/mol at $\bar{n} = 10$ to -50 ± 15 kJ/mol at $\bar{n} = 2$. Thus the water at lower degrees of hydration appears to be more tightly bound. Though the uncertainties in $\Delta \bar{h}_{H_2O}$ are large (± 10 to ± 15 kJ/mol), this variation appears to be outside of experimental error. These partial molar enthalpies of hydration define a straight line (see Fig. 6) which gives (in kJ/mol)

$$\Delta \bar{h}_{H_2O} = -57.21 + 3.68 \ n \quad (7)$$

This linear behavior of $\Delta \bar{h}_{H_2O}$ calculated point by point suggests that one is justified in fitting all the transposed temperature drop calorimetric data for this sample to a second-order polynomial. This gives, with DH_{TTD} in kJ/mol

$$\Delta H_{TTD} = 528.22 \ (\pm 13.03) + 122.07 \ n \ (\pm 4.74) -1.47 \ (\pm 0.34) \ n^2,$$
$$r = 0.9 \ 97 \quad (8)$$

Other measures (analysis of variance, Durbin-Watson statistics) suggest that the quadratic fit is statistically significant. The integral enthalpy of hydration (per mole liquid H_2O) from the quadratic fit is -34.6 ± 1.2 kJ/mol, in good agreement with the linear fit (-33.0 ± 1.2 kJ/mol). Figure 5 suggests that the quadratic fit gives a better representation of the data at high n ($n = 9$–12.5) but gives substantial downward curvature at low n, leading to a significantly smaller heat content calculated for anhydrous CHA, 528.7 ± 13.0 kJ/mol for the quadratic fit compared to 573.9 ± 8.8 kJ/mol for the linear fit. Thus preference for the quadratic fit must be taken with some caution, and is based on physical insight as well as statistics. For the quadratic fit, the partial molar enthalpy of hydration, $\Delta \bar{h}_{H_2O}$ (in kJ/mol relative to liquid water) is:

$$\Delta \bar{h}_{H_2O} = -52.97 \ (\pm 4.74) + 2.94 \ (\pm 0.68) \ n \quad (9)$$

This is quite similar to Equation 7 derived from taking pairs of individual data points. We conclude it is highly probable that the partial molar enthalpy of hydration becomes less exothermic with increasing water content.

The linear variation in $\Delta \bar{h}_{H_2O}$ suggests that dehydration is not stepwise. This is supported by the TGA/DTA curve which shows continuous H_2O release.

These results may be compared to several other studies of Ca-zeolite hydration energetics. Valueva and Goryainov (1992) studied hydration of natural chabazite by immersion calorimetry and Raman spectroscopy and determined the partial en-

TABLE 6. Calculation of partial molar enthalpy of hydration of Ca -CHA (084-32)

n_1	n_2	$\bar{n}$	Δn	$\Delta H_{TTD}(1)$ (kJ/mol)	$\Delta H_{TTD}(2)$ (kJ/mol)	$\Delta \bar{h}_{H_2O}$ (kJ/mol)
1.044	3.177	2.111	2.133	654.0 ± 7.3	907.7 ± 30.9	−49.8 ± 14.9
2.635	4.975	3.805	2.340	832.0 ± 18.2	1098.5 ± 14.7	−44.8 ± 10.0
3.177	7.655	5.416	4.478	907.7 ± 30.9	1370.5 ± 30.0	−34.3 ± 9.6
4.975	9.294	7.135	4.319	1098.5 ± 14.7	1542.8 ± 20.2	−33.8 ± 5.8
7.655	11.677	9.666	4.022	1370.5 ± 30.0	1749.9 ± 31.5	−25.2 ± 10.8
9.294	12.540	10.917	3.246	1542.8 ± 20.2	1814.8 ± 12.7	−14.7 ± 7.4
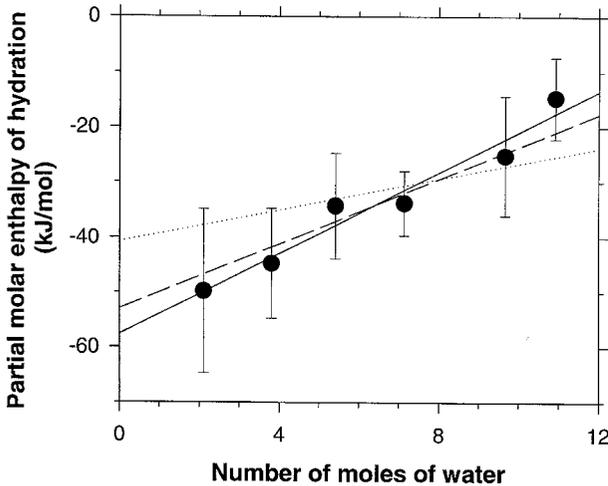
FIGURE 6. The partial molar enthalpy of hydration (relative to liquid water) of Ca-CHA (084-32) as a function of water content, calculated by taking differences between alternate pairs of enthalpies of transposed temperature drop (see text). The circles with error bars represent the point by point calculation described in text. The solid line is a least squares fit to these points (Eq. 7). The dashed line is from a quadratic fit to ΔH_{TTD} (Eqs. 8 and 9). The dotted line is from a quadratic fit to the data of Valueva and Goryainov (1992) (Eq. 9).

thalpy of hydration. Their enthalpy data show a qualitative trend similar to ours. Their integral heat of rehydration vs. water content shows curvature, but also considerable scatter, with water content. This is consistent with a linear dependence on n of the partial molar enthalpy of hydration. However, they chose to separate the data into three regions: n = 0 to 1.7, $\Delta \bar{h}_{H_2O} = -30 \pm 5$ kJ/mol; n = 1.7 to 3.8, $\Delta \bar{h}_{H_2O} = -72 \pm 9$ kJ/mol; and n = 4 to 7, $\Delta \bar{h}_{H_2O} = -39 \pm 4$ kJ/mol, referred to liquid water. The spectroscopic data, on which Valueva and Goryainov base their stepwise model, may reflect kinetic control of dehydration. We suggest that the separation of $\Delta \bar{h}_{H_2O}$ into three regions of differing but constant hydration enthalpy may be an overinterpretation of the data.

The immersion calorimetric data of Valueva and Goryainov (1992) can be fit to a single quadratic polynomial representing the integral enthalpy of hydration from n = 0 to n = 7. This polynomial gives the partial molar enthalpy of water, $\Delta \bar{h}_{H_2O}$, relative to liquid water, as

$$\Delta \bar{h}_{H_2O} = -40.7 + 1.408\ n\ \text{(kJ/mol)} \quad (10)$$

This gives an average enthalpy of hydration of −32.3 kJ/mol. Thus their data can be treated to obtain results reasonably similar to ours.

Carey and Bish (1997) determined the energetics of clinoptilolite hydration by both water equilibration and by immersion calorimetry. Although the chabazite framework is different from that of clinoptilolite, because the hydration process mainly involves the extra-framework cations, it is interesting to compare the two systems. Their calorimetric data for clinoptilolite showed a linear dependence of $\Delta \bar{h}_{H_2O}$ on water content, with $\Delta \bar{h}_{H_2O} = -58$ kJ/mol (liquid water reference state) for the dehydrated sample and $\Delta \bar{h}_{H_2O} = -4$ kJ/mol for the fully hydrated sample. Their thermogravimetric data suggested a quadratic relation of $\Delta \bar{h}_{H_2O}$ vs. fractional water content, with $\Delta \bar{h}_{H_2O} = -76$ kJ/mol for the dehydrated sample and $\Delta h_{H_2O} = -16$ kJ/mol for the fully hydrated clinoptilolite. In either case, the data for Ca-clinoptilolite and Ca-chabazite are similar in that both show that the partial molar enthalpy of hydration becomes less exothermic with increasing water content. This dependence appears more pronounced for clinoptilolite than for chabazite, but kinetic as well as thermodynamic factors may play a role. The average enthalpies of hydration (−30.3 ± 2.0 kJ/mol for Ca-clinoptilolite and −33.1 ± 1.2 kJ/mol for Ca-chabazite, liquid water standard state) are very similar. Both chabazite and clinoptilolite show continuous dehydration with a linearly varying enthalpy, rather than stepwise behavior.

It is appropriate to compare the different methodologies for obtaining hydration energetics. The temperature dependence of equilibrium isotherms divides the free energy into enthalpy and entropy terms. In general the accessible temperature range is small and the data analysis is model dependent (Carey and Bish 1996). Kinetic and thermodynamic effects may be intermingled. Thus overall accuracy is hard to judge. DSC/TGA gives details of water loss as a function of temperature. Kinetic and thermodynamic effects cannot be separated, especially when "steps" or "two-phase regions" appear to be seen in the dehydration. Quantitative enthalpies of hydration are difficult to obtain. Immersion calorimetry, in which a partially dehydrated sample is rehydrated in water (Valueva and Goryainov 1992; Carey and Bish 1997), can be very accurate, as can methods that "titrate" a dehydrated sample with aliquots of water vapor (McHale et al. 1997). Immersion calorimetry is an integral measurement (partially hydrated → fully hydrated), whereas titration calorimetry gives the partial molar enthalpy of hydration directly. Solution calorimetry, whether in acid (Johnson et al. 1982, 1992) or in oxide melts (Kiseleva et al. 1996a) provides the enthalpy of hydration as the difference in enthalpy of formation of hydrous and anhydrous samples. Transposed temperature drop calorimetry, as done in this study, can

be used to obtain partial molar enthalpies of hydration, though generally with lower accuracy than the immersion and vapor "titration" methods. An advantage of the high-temperature method is the rapid attainment of the final state at 700 °C, making kinetic concerns unimportant. We believe that a combination of these various methods should be used in the future. Together, they can address whether a state of intermediate hydration is defined uniquely by its water content, or whether it is path dependent, varying with direction (hydration or dehydration), heating rate, and other parameters. These questions are crucial to understanding mechanisms and the meaning of "steps" seen in heating studies. Furthermore, calorimetric and structural studies on the same samples should be pursued simultaneously.

Structural changes during dehydration and their energetic significance

Even when a zeolite framework is maintained during dehydration, the small peak shifts seen in XRD patterns suggest that the framework, the cations, and the remaining water molecules do relax during dehydration. Because of the small and subtle nature of such changes and the difficulty in maintaining a constant hydration state during structural studies, there have been few detailed investigations of the structure of partially dehydrated zeolites.

Several structural studies of zeolites have proposed distinct ordered hydration steps (clinoptilolite: Armbruster and Gunter 1991; faujasite: Dooryhee et al. 1991; laumontite: Armbruster and Kohler 1992; chabazite: Valueva and Goryainov 1992). It is suggested that cations are coordinated by framework oxygen atoms in the dehydrated structure, but in the fully hydrated material, cations have a complete coordination sphere of water as they float inside the cage. Raman spectroscopic studies of chabazite during dehydration (Valueva and Goryainov 1992) suggest stepwise changes in the binding of water.

Structural studies using EXAFS show the coexistence of several cation coordination states during hydration (Dooryhee et al. 1991). Their results demonstrate that even using synchrotron XRD, site determination by Rietveld refinement was different from that by EXAFS. The latter may be more sensitive to the local coordination state. It is clear that more-detailed structural studies of partially hydrated (and potentially disordered) samples would be useful.

During hydration, the zeolite framework may change in response to the position of cations and H_2O molecules (Smith 1962; Smith and Rinaldi 1963; Mortier et al. 1977). In the dehydrated state, strain may be induced in the chabazite framework by extra-framework cations that are close to the framework oxygen atoms. As water is gained, the cation may displace to the center of its cage, reduce its coordination to framework oxygen atoms, and reduce strain. This coupled process may decrease the difference in energetics at different degrees of hydration and introduce considerable cooperativity into the hydration process.

Indeed, the site occupancy of Ca in chabazite may be different in hydrated and dehydrated samples, with site I (D6R) unoccupied in the hydrated sample but occupied in the dehydrated material (Smith et al. 1964). The coupling of cation lo-

cation and hydration state may further complicate the energetics. According to the siting exclusion principle for sites I and II in Ca chabazite (Mortier et al. 1977), 40% of the site I positions (D6R) should be occupied by Ca^{2+} in a dehydrated sample with Si/Al = 2.7. This represents about 25% of the Ca. The other Ca cations are on site II (S6R) in the chabazite cage. As water enters the material, the Ca in the chabazite cage will become hydrated and move off the S6R site. This allows site I Ca to migrate out of D6R and become hydrated (Smith et al. 1964). The site I calcium acts as a reservoir of dehydrated cations, which, after some level of partial hydration, migrate from the D6R site into the chabazite cage, thereby replenishing the supply of dehydrated cations and perhaps resulting in a redistribution of the molecules of hydration. This may contribute to the smooth, rather than stepwise, hydration energetics. Whether a given zeolite will show gradual or stepwise loss of water on heating is a function of both thermodynamic and kinetic factors. Thermodynamically, it is related to the energetics of dehydration—whether the partial molar enthalpy of hydration varies smoothly with water content or whether two distinct phases of different water content and structure coexist, such as laumontite-leonhardite. Kinetically, heating rate, external water fugacity, and particle size may all play a role. At present the structural data that are needed for understanding the microscopic basis of differences in macroscopic hydration behavior are still rather fragmentary.

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APPENDIX 1: THERMOCHEMICAL CYCLES USED IN CALCULATIONS

A. Enthalpy of formation from oxides at 25 °C of hydrated sample 084-27

$$\frac{3.27}{2}\text{Li}_2\text{O (xl, 25 °C)} = \frac{3.27}{2}\text{Li}_2\text{O (sol, 700 °C)} \quad (1)$$

$$\frac{0.62}{2}\text{Na}_2\text{O (xl, 25 °C)} = \frac{0.62}{2}\text{Na}_2\text{O (sol, 700 °C)} \quad (2)$$

$$\frac{0.02}{2}\text{K}_2\text{O (xl, 25 °C)} = \frac{0.02}{2}\text{K}_2\text{O (sol, 700 °C)} \quad (3)$$

$$\frac{3.96}{2}\text{Al}_2\text{O}_3\text{ (xl, 25 °C)} = \frac{3.96}{2}\text{Al}_2\text{O}_3\text{ (sol, 700 °C)} \quad (4)$$

$$8.04\ \text{SiO}_2\text{ (xl, 25 °C)} = 8.04\ \text{SiO}_2\text{ (sol, 700 °C)} \quad (5)$$

$$12.59\ \text{H}_2\text{O (l, 25 °C)} = 12.59\ \text{H}_2\text{O (g, 700 °C)} \quad (6)$$

$$\frac{3.27}{2}\text{Li}_2\text{O(sol, 700 °C)} + \frac{0.62}{2}\text{Na}_2\text{O(sol, 700 °C)}$$
$$+ \frac{0.02}{2}\text{K}_2\text{O(sol, 700 °C)} + \frac{3.96}{2}\text{Al}_2\text{O}_3\text{(sol, 700 °C)}$$
$$+ 8.04\text{SiO}_2\text{(sol, 700 °C)} + 12.59\ \text{H}_2\text{O(g, 700 °C)}$$
$$= \text{Li}_{3.27}\text{Na}_{0.62}\text{K}_{0.02}\text{Al}_{3.96}\text{Si}_{8.04}\text{O}_{24}\cdot 12.59\text{H}_2\text{O(xl, 25 °C)}$$
$$(7)$$

$$\frac{3.27}{2}\text{Li}_2\text{O(xl, 25 °C)} + \frac{0.62}{2}\text{Na}_2\text{O(xl, 25 °C)}$$
$$+ \frac{0.02}{2}\text{K}_2\text{O(xl, 25 °C)} + \frac{3.96}{2}\text{Al}_2\text{O}_3\text{(xl, 25 °C)}$$
$$+ 8.04\text{SiO}_2\text{(xl, 25 °C)} + 12.59\ \text{H}_2\text{O(l, 25 °C)}$$
$$= \text{Li}_{3.27}\text{Na}_{0.62}\text{K}_{0.02}\text{Al}_{3.96}\text{Si}_{8.04}\text{O}_{24}\cdot 12.59\text{H}_2\text{O(xl, 25 °C)}$$
$$(8)$$

$$\Delta H_8 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7$$

B. Enthalpy of formation from the oxides at 700 °C of dehydrated sample 084-27

$$\frac{3.27}{2}\text{Li}_2\text{O (xl, 700 °C)} = \frac{3.27}{2}\text{Li}_2\text{O (sol, 700 °C)} \quad (1)$$

$$\frac{0.62}{2}\text{Na}_2\text{O (xl, 700 °C)} = \frac{0.62}{2}\text{Na}_2\text{O (sol, 700 °C)} \quad (2)$$

$$\frac{0.02}{2}\text{K}_2\text{O (xl, 700 °C)} = \frac{0.02}{2}\text{K}_2\text{O (sol, 700 °C)} \quad (3)$$

$$\frac{3.96}{2}\text{Al}_2\text{O}_3\text{ (xl, 700 °C)} = \frac{3.96}{2}\text{Al}_2\text{O}_3\text{ (sol, 700 °C)} \quad (4)$$

$$8.04\ \text{SiO}_2\text{ (xl, 700 °C)} = 8.04\ \text{SiO}_2\text{ (sol, 700 °C)} \quad (5)$$

$$\frac{3.27}{2}\text{Li}_2\text{O(sol, 700 °C)} + \frac{0.62}{2}\text{Na}_2\text{O(sol, 700 °C)}$$
$$+\frac{0.02}{2}\text{K}_2\text{O(sol, 700 °C)} + \frac{3.96}{2}\text{Al}_2\text{O}_3\text{(sol, 700 °C)}$$
$$+8.04\text{SiO}_2\text{(sol, 700 °C)}$$
$$= \text{Li}_{3.27}\text{Na}_{0.62}\text{K}_{0.02}\text{Al}_{3.96}\text{Si}_{8.04}\text{O}_{24}\text{(xl, 700 °C)} \quad (6)$$

$$\frac{3.27}{2}\text{Li}_2\text{O(xl, 700 °C)} + \frac{0.62}{2}\text{Na}_2\text{O(xl, 700 °C)}$$
$$+\frac{0.02}{2}\text{K}_2\text{O(xl, 700 °C)} + \frac{3.95}{2}\text{Al}_2\text{O}_3\text{(xl, 700 °C)}$$
$$+8.05\text{SiO}_2\text{(xl, 700 °C)} + 12.59\ \text{H}_2\text{O(l, 700 °C)}$$
$$= \text{Li}_{3.27}\text{Na}_{0.62}\text{K}_{0.02}\text{Al}_{3.95}\text{Si}_{8.05}\text{O}_{24}\text{(xl, 700 °C)} \quad (7)$$

$$\Delta H_7 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$$

C. Calculation of integral enthalpy of hydration

$$\text{CHA(700 °C)} + n\text{H}_2\text{O(gas, 700 °C)} = \text{CHA} \cdot n\text{H}_2\text{O (25 °C)} \quad (1)$$

$$\text{CHA(25 °C)} = \text{CHA(700 °C)} \quad (2)$$

$$n\text{H}_2\text{O(l, 25 °C)} = n\text{H}_2\text{O(g, 700 °C)} \quad (3)$$

$$\text{CHA(25 °C)} + n\text{H}_2\text{O(l, 25 °C)} = \text{CHA} \cdot n\text{H}_2\text{O(25 °C)} \quad (4)$$

$$\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_{\text{hydration}} = \Delta H_4 / n$$

D. Calculation of partial molar enthalpy of hydration

$$\text{CHA} \cdot n_1\text{H}_2\text{O(25 °C)} = \text{CHA(700 °C)} + n_1\text{H}_2\text{O(g, 700 °C)} \quad (1)$$

$$\text{CHA(700 °C)} + n_2\text{H}_2\text{O(g, 700 °C)} = \text{CHA} \cdot n_2\text{H}_2\text{O(25 °C)} \quad (2)$$

$$(n_2 - n_1)\text{H}_2\text{O(l, 25 °C)} = (n_2 - n_1)\text{H}_2\text{O(g, 700 °C)} \quad (3)$$

$$\text{CHA} \cdot n_1\text{H}_2\text{O(25 °C)} + (n_2 - n_1)\text{H}_2\text{O(l, 25 °C)} \quad (4)$$
$$= \text{CHA} \cdot n_2\text{H}_2\text{O(25 °C)}$$

$$\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta \bar{h}_{\text{H}_2\text{O}} = \Delta H_4 / (n_2 - n_1)$$

APPENDIX 2: HEAT CONTENTS OF ANHYDROUS ZEOLITE FRAMEWORKS

To calculate integral and average enthalpies of hydration from transposed temperature drop calorimetry data by thermochemical cycle C in Appendix 1, one needs values for the heat content ($H_{700\,°C} - H_{25\,°C}$) of the dehydrated zeolite framework. In principle this could be measured by transposed temperature drop calorimetry of the dehydrated sample, but two difficulties arise. A minor difficulty (because the heat content is not strongly affected by it) is the partial amorphization of the dehydrated samples. A major difficulty is the very ready rehydration of the dehydrated samples, as described in the section on preparation of partially hydrated samples. Thus maintaining a completely anhydrous sample for TTD experiments was not possible.

The heat content of a framework silicate reflects its vibrational heat capacity. Petrovic et al. (1993) showed that the heat content of a series of SiO_2 zeolites (and also cristobalite and silica glass) varied little, changing by ~1 kJ/mol (two oxygen basis) with framework density. Similarly, the heat content of feldspars and glass of the same composition is similar (Robie and Hemingway 1995) and the heat contents of Na-faujasites of varying Al contents are similar to these of glasses of the same composition [comparing data in Petrovic and Navrotsky (1997) and Robie and Hemingway (1995)]. Thus the major factor controlling heat capacity and heat content is composition rather than the structure of the framework. The heat content, per $M_x(Al_ySi_{1-y})O_2$ formula unit (M = alkali or alkaline earth), depends most strongly on the number of atoms (per two oxygen formula) contributing to the vibrations, and to a smaller extent, on the nature of the cations. Thus a plot of heat content (per two O atoms formula unit) vs. total extra-framework cation content should, to a first approximation, yield a straight line. Appendix 2 Figure 1 shows this relation. Although the data show some scatter, there is no strong distinction between dense crystalline framework, glass, and zeolite, or between different cations. The expected linear relation between heat con-

tent and extra-framework cation content is confirmed, and gives (kJ/mol):

$$H_{700\,°C} - H_{25\,°C} = 41.67 + 23.78 \text{ x, r} = 0.967 \qquad (1)$$

where x is the number of extra-framework cations per TO_2.

Using the cation content rather than the Al content is important when comparing cations of different charges. Thus $Ca_{0.5}Al_{0.5}Si_{0.5}O_2$ has the same number of atoms and number of vibrational modes as $NaAl_{0.25}Si_{0.75}O_2$ and these two have similar heat contents, but different Al/(Al + Si) values.

For the Ca-CHA sample 084-32 studied in detail in this work, the above correlation predicts a heat content of 544.3 kJ/mol (24 oxygen basis). Using this value in thermochemical cycle C in Appendix 1 gives an average enthalpy of hydration of –32.7 kJ/mol per mole of liquid water. From the TTD data on partially hydrated samples (Table 2), a linear fit gives a heat content of 573.9 kJ/mol and an average enthalpy of hydration of –33.1 kJ/mol. A quadratic fit gives a heat content of 528.7 kJ/mol and an average hydration enthalpy of –34.3 kJ/mol. It is interesting that the heat contents from the linear and quadratic fits bracket the predicted value. It is encouraging that the average enthalpies of hydration are similar in all cases. The correlation seen in Figure A2-1 (Eq. 1) can then be used in the thermodynamic cycle to calculate average heats of hydration for all samples studied, with results shown in Table 3 and Figure 4. Considering all sources of error, we estimate the uncertainty in the calculated average enthalpy of hydration to be ± 4 kJ/mol.
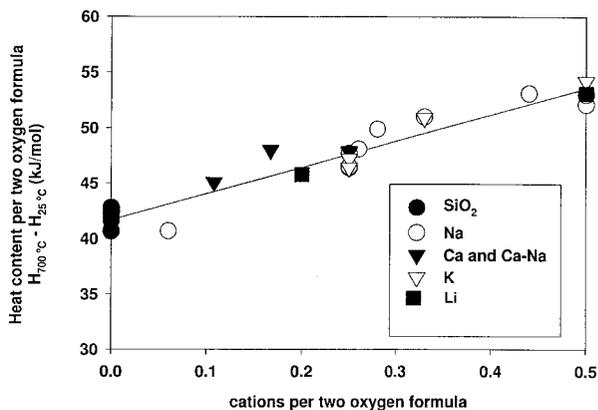
APPENDIX 2—FIGURE 1. Heat content, $(H_{700\,°C} - H_{25\,°C})$ in kJ per two oxygen formula unit as a function of cation content x, in $M_x(Si_{1-y}Al_y)O_2$ framework silicates. Data include dehydrated zeolites, glasses, and dense framework materials. Line is least-squares fit. Data include cristobalite and SiO_2 glass (Robie and Hemingway 1995), SiO_2 zeolites (Petrovic et al. 1993); high- and low-albite and $NaAlSi_3O_8$ glass (Robie and Hemingway 1995), nepheline and $NaAlSiO_4$ glass (Robie and Hemingway 1995), microcline, sanidine, and $KAlSi_3O_8$ glass (Robie and Hemingway 1995), kaliophillite, leucite, b-eucryptite, and petalite (Robie and Hemingway 1995), dehydrated leonhardite (Kiseleva et al. 1996a), dehydrated analcime (Robie and Hemingway 1995), several Na-faujasites of various Si/Al ratios (Petrovic and Navrotsky 1997), and dehydrated mordenite (Johnson et al. 1992).