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The molar enthalpy of dehydration of cordierite

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ABSTRACT

The molar enthalpy of dehydration of hydrous cordierite ($Mg_2Al_4Si_5O_{18} \cdot nH_2O$) was determined by transposed temperature drop calorimetry. Six samples ranging from 0 to 0.84 H_2O per formula unit were examined. The observed enthalpy of dehydration is a linear function of H_2O content indicating an ideal enthalpy of mixing for H_2O in cordierite. The molar enthalpy of dehydration is 41.8 ± 1.6 kJ/mol at the reference conditions 25 °C, 1 bar, and gaseous H_2O. This value is the same as the molar enthalpy of vaporization for water (40.9 kJ/mol) within experimental uncertainty and is considerably less than that found for the dehydration of zeolites (61–84 kJ/mol).

INTRODUCTION

Cordierite is a framework aluminosilicate with the zeolite-like capacity to adsorb molecular H_2O. The adsorption of H_2O enhances the stability of cordierite relative to less hydrous minerals, but this effect has not been well quantified. In contrast to the H_2O in most zeolites, the H_2O in cordierite occurs on a well-defined crystallographic site and does not hydrate cations. Knowledge of the energetics of dehydration of cordierite would provide a useful end-member for models of the thermodynamic behavior of H_2O in zeolites.

A general chemical formula for natural cordierite is $(Mg,Fe)_2Al_4Si_5O_{18} \cdot nH_2O$. Analyses of natural cordierite commonly show from 0.5 to 2.5 wt% H_2O corresponding, approximately, to values of n from 0.17 to 0.84 (Deer et al., 1986). The H_2O molecules are located in the center of small cages that occur in chains parallel to the **c** axis (Gibbs, 1966). The cages are bounded by sixfold tetrahedral rings and have a probable maximum occupancy of a single H_2O molecule, equivalent to $n = 1$. However, synthetic cordierite with a maximum value of $n = 1.3$ has been produced at low temperature and high pressure (Mirwald et al., 1979), and Leake (1960), in a literature survey, reported several analyses of natural cordierite with values of n greater than 1 and as high as 1.67.

The environment of H_2O in cordierite and zeolites differs in two important ways. The H_2O molecules in cordierite are coordinated by O ions of the framework and possibly by H_2O molecules in adjacent cages. They are not coordinated by the divalent cations (Mg^{2+}, Fe^{2+}), which are confined to octahedra that help link the cages together. This is in contrast to the zeolites, in which the H_2O molecules occur together with the charge-balancing cations in the cages. In addition, most zeolite cages are sufficiently large that the H_2O molecules do not occupy well-constrained crystallographic sites.

Cordierite is a common mineral in metamorphosed mudstones, in altered, mafic metavolcanic rocks, and in peraluminous igneous rocks. It is involved in a number of equilibria that are sensitive indicators of petrogenetic processes (e.g., Thompson, 1976; Holdaway and Lee, 1977; Herzberg, 1983). These equilibria are difficult to interpret with confidence because of the uncertain role that H_2O plays in stabilizing cordierite. Important constraints are provided by experimental syntheses of hydrous cordierite (e.g., Schreyer and Yoder, 1964; Mirwald et al., 1979). In these studies, anhydrous cordierite adsorbs H_2O at conditions ranging from 400 to 1000 °C and 0.5 to 11 kbar P_{H_2O}. A number of attempts to obtain a thermodynamic formulation of the cordierite-H_2O system have been made with these data (e.g., Newton and Wood, 1979; Lonker, 1981; Martignole and Sisi, 1981; Bhattacharya and Sen, 1985; McPhail et al., 1990). Many of these account for the synthesis data reasonably well, but the formulations are poorly constrained because few calorimetrically determined properties of hydrous cordierite are known.

This report presents the results of transposed temperature drop calorimetry on a series of synthetic magnesium cordierite samples with different H_2O contents. The data are used to obtain the molar enthalpies of dehydration and the enthalpy of formation of hydrous cordierite ($n = 1$). The molar enthalpy of dehydration is near the molar enthalpy of vaporization of water and is considerably lower than that found in many zeolites. Some of these results have been discussed previously in Carey (1990a, 1990b) and Carey and Navrotsky (1991).

EXPERIMENTAL METHODS

Sample preparation

The synthesis and characterization procedures for cordierite will be described briefly. A more complete de-

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TABLE 1. Composition of synthetic cordierite

Oxide	Glass (37)	Anhydrous (14)	Hydrous (28)
SiO_2	51.21	51.21	49.94
Al_2O_3	35.05	34.78	33.59
MgO	13.29	13.35	13.17
FeO_{tot}	0.03	0.03	0.02
CaO	0.06	0.06	0.05
MnO	0.01	0.00	0.01
Na_2O	0.10	0.10	0.09
K_2O	0.01	0.02	0.02
Total	99.76	99.56	96.89
	Cations per 18 O atoms		
Si	4.999	5.010	5.020
Al	4.032	4.010	3.979
Mg	1.934	1.947	1.973
Fe	0.002	0.002	0.001
Ca	0.007	0.006	0.006
Mn	0.001	0.000	0.001
Na	0.019	0.019	0.016
K	0.001	0.001	0.002
Total	10.995	10.995	10.998

Note: The number of analyses is given in parentheses. The anhydrous cordierite was annealed 100 h, and the hydrous cordierite was derived from the syntheses at 2 and 3 kbar.

TABLE 2. Synthesis results of hydrous cordierite

	1 – 200 mesh		2 – 325 mesh	
Pressure (bars)	Wt% H_2O*	Range**	Wt% H_2O*	Range**
100	0.41(4)	0.37–0.51	0.49(4)	0.42–0.60
500	0.99(4)	0.95–1.07	1.05(5)	0.99–1.13
1000	1.34(5)	1.33–1.36	1.35(4)	1.33–1.37
3000	1.99(4)	1.90–2.05	1.92(4)	1.86–2.00
5750	2.52(3)	2.45–2.56	2.46(2)	2.44–2.47

* Average value with the number of distinct syntheses in parentheses.
** Total range of synthesis results.

scription is given in Carey (1990b). Anhydrous and hydrous magnesium cordierite were prepared following procedures discussed by Schreyer and Schairer (1961) and Schreyer and Yoder (1964). Anydrous magnesium cordierite was obtained by first melting a stoichiometric mix of the oxides at a temperature in excess of 1550 °C to form 1 kg of glass in the shape of a rectangular slab. A portion of the glass was crystallized in a 1-atm furnace at 1250 °C for a period of 200 h. The compositions of the glass and the anhydrous cordierite, as determined by electron microprobe, are shown in Table 1. Both materials were homogeneous, with a nearly stoichiometric composition. The cordierite contained minor foreign crystals observable with an optical microscope (<3 modal% of <1-μm needles of mullite or sillimanite and beads of quartz?). X-ray diffraction revealed only orthorhombic cordierite with a Miyashiro distortion index of 0.20. The crystallization and annealing process was sufficient, according to Putnis et al. (1987), to produce an essentially completely ordered distribution of Al and Si.

To make hydrous cordierite, the anhydrous material was gently crushed and sieved to two mesh fractions of 75–150 and 25–75 μm and combined with H_2O in Au capsules. The capsules were welded and placed in hydrothermal pressure vessels at 600 °C and at pressures ranging from 100 bars to 5.75 kbar for a period of 4 d. The samples were quenched by isolating the vessels from the pressure line and placing them in a stream of compressed air. (These conditions approximate a constant volume cooling path.) All of the syntheses were conducted within the stability field of cordierite, according to Schreyer and Yoder (1964), as well as others. The nonvolatile composition of the hydrous cordierite, as determined by electron microprobe, is shown in Table 1. The H_2O content of cordierite was determined by thermogravimetry at 1000 °C, with results given in Table 2. At this temperature, cordierite loses its H_2O rapidly (in less than a few minutes for the grain size used here). The thermogravimetric results were checked by melting a sample of hydrous cordierite, with a resulting mass loss essentially the same as that determined by thermogravimetry. The hydrous cordierite showed evidence of recrystallization and grain growth in observations by SEM, but no evidence of cordierite breakdown to other phases was detected by SEM, optical, or X-ray diffraction observations. We assumed that some of the capsules leaked on the basis of mass changes in the sample charge. As no detectable difference in the amount of H_2O, the composition, or morphology of the cordierite was observed in the leaky samples, these materials were also used in the calorimetric experiments. The speciation of H_2O in cordierite was examined by Fourier-transform IR spectroscopy. Most of the H_2O is in the type-I orientation of Goldman et al. (1977) as is expected from the low Na content of the synthetic cordierite. However, small absorption peaks due to type-II H_2O were also present.

Calorimetric methods

A Calvet-type calorimeter was used in the study and was operated at 784 °C as a transposed temperature-drop calorimeter without oxide solvent. The calorimeter has been described by Navrotsky (1977). A flowing-Ar atmosphere in the calorimeter prevented shifts in the base line due to the liberation of H_2O from cordierite (Rapp and Navrotsky, 1990). The measurements were performed by dropping a sample at room temperature (22 °C) into the calorimeter at 784 °C. The calorimeter records the enthalpy change necessary to heat the sample from room temperature to 784 °C, plus the enthalpy of any phase change or chemical reaction that has occurred in that interval.

The calorimeter was calibrated by dropping 30–50 mg samples of synthetic corundum in loosely crimped, preannealed Pt capsules of 35–55 mg. The standard enthalpy changes for these materials were taken from Robie et al. (1978). The cordierite samples ranged in size from 30 to 80 mg and were also dropped in loosely crimped, preannealed Pt. Approximately 10–15 min were required for complete outgassing of cordierite at 784 °C, as judged from the return of the instrument to a stable base line. This time period is consistent with the kinetic experi-

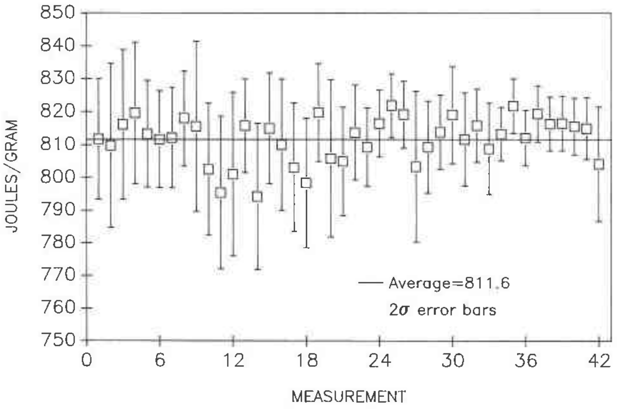

Fig. 1. Measurements of the enthalpy change in anhydrous cordierite on passing from 22 to 784 °C. The data are presented in the sequence taken, with error bars representing the estimated 2σ uncertainty normalized to the mass of cordierite.

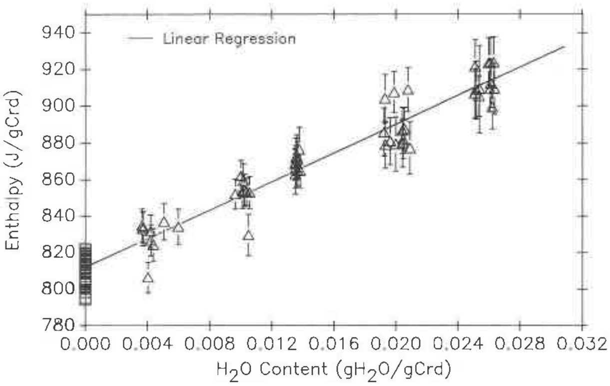

Fig. 2. Measurements of the enthalpy change from 22 to 784 °C in anhydrous and hydrous cordierite as a function of the H_2O content. The error bars represent the estimated 2σ uncertainty normalized to the mass of anhydrous cordierite.

ments of Carey (1990b), using thermogravimetric methods at 784 °C.

RESULTS

Thermochemical cycle

The dehydration of cordierite is represented by the following reaction:

$$Mg_2Al_4Si_5O_{18}\cdot nH_2O = Mg_2Al_4Si_5O_{18} + nH_2O(\text{gas}). \quad (1)$$

The calorimetric measurements were designed to yield the enthalpy of Reaction 1 as a function of n (moles of H_2O per formula unit of cordierite) at the reference conditions of room temperature (22 °C), 1 bar, and gaseous H_2O. This enthalpy was determined as the sum of the thermochemical cycle shown in Table 3. Reaction 2 of Table 3 is the enthalpy change of hydrous cordierite from 22 to 784 °C determined by transposed temperature drop calorimetry. Reaction 3 is the enthalpy change of anhydrous cordierite also determined by transposed temperature drop calorimetry. Reaction 4 is the enthalpy change of pure gaseous H_2O from 784 to 22 °C at 1 bar and was obtained from the tabulation of Robie et al. (1978). The sum of these reactions yields the enthalpy of Reaction 1.

Anhydrous cordierite

The enthalpy change of anhydrous cordierite from 22 to 784 °C (the opposite of Reaction 3) was determined as the average of the 42 measurements shown in Figure 1. The data are presented in the order collected, with error bars corresponding to the estimated 2σ uncertainty in the measurements normalized to the mass of the anhydrous cordierite sample. The standard deviation of the measurements is 6.968 J/g or 0.8% of the average value, which is near the typical standard deviation of the calibration measurements. The measured enthalpy change of Reaction 3 is −811.604 ± 1.075 J/g, where the uncertainty is the standard error of the measurement. (The data are reported with more digits than are significant to avoid round-off errors in the calculations.) This enthalpy value may be compared with that obtained by Pankratz and Kelley (1964) using conventional drop calorimetry of −811.786 J/g as formulated by Robie et al. (1978).

TABLE 3. Thermochemical cycle used to obtain the molar enthalpy of dehydration of cordierite

Reaction	Equation
$Mg_2Al_4Si_5O_{18}\cdot nH_2O$ (22 °C) = $Mg_2Al_4Si_5O_{18}$ (784 °C) + nH_2O (784 °C)	(2)
$Mg_2Al_4Si_5O_{18}$ (784 °C) = $Mg_2Al_4Si_5O_{18}$ (22 °C)	(3)
nH_2O (784 °C) = nH_2O (22 °C, gas)	(4)
$Mg_2Al_4Si_5O_{18}\cdot nH_2O$ (22 °C) = $Mg_2Al_4Si_5O_{18}$ (22 °C) + nH_2O (22 °C, gas)	(1)

Hydrous cordierite

The enthalpy change of hydrous cordierite from 22 to 784 °C (Reaction 2) was determined by 51 measurements of hydrous cordierite combined with the anhydrous data as shown in Figure 2 and listed in Table 4. The enthalpy change is reported in J/g of anhydrous cordierite as a function of the H_2O content in grams of H_2O per gram of anhydrous cordierite (g-H_2O/g-Crd). The error bars are equivalent to the estimated 2σ uncertainty of the measurements normalized to the mass of anhydrous cordierite. The data fall into six groups corresponding to separate synthesis conditions ranging from 1 bar (0 g-H_2O/g-Crd) to 5.75 kbar (~0.027 g-H_2O/g-Crd).

The data for hydrous cordierite are consistent with a linear trend in the enthalpy of dehydration as a function of H_2O content. A linear regression involving all of the data points (hydrous and anhydrous) results in the following relationship:

$$\begin{aligned}\Delta H_{\text{rxn}}\ (\text{J/g-Crd}) = {} & 3901.065\ (\text{J/g-H}_2\text{O}) \\ & \times n\ (\text{g-H}_2\text{O/g-Crd}) \\ & + 811.979\ (\text{J/g-Crd}). \quad (5)\end{aligned}$$

The correlation coefficient of the regression is 0.9776,

Table 4. Results of the enthalpy measurements on hydrous cordierite

Total mass (mg)	Anhy. crd (mg)	H_2O (mg)	Enthalpy (J/g-Crd)	Wt% H_2O
28.30	27.60	0.70	886.62	2.47
63.00	62.16	0.84	854.37	1.33
42.38	41.34	1.04	886.24	2.45
61.33	60.51	0.82	859.97	1.34
47.99	46.77	1.22	899.90	2.54
70.32	69.38	0.94	857.48	1.34
55.32	53.92	1.41	885.88	2.54
78.88	77.82	1.06	853.18	1.34
51.49	50.18	1.31	888.85	2.54
76.71	75.69	1.02	856.97	1.33
48.60	47.37	1.23	899.95	2.53
86.84	85.95	0.89	844.47	1.02
57.56	56.09	1.47	876.22	2.55
58.78	58.17	0.61	820.93	1.04
48.71	47.46	1.25	885.84	2.57
74.66	73.88	0.78	843.98	1.04
47.61	46.39	1.22	899.95	2.56
74.09	73.34	0.75	845.37	1.01
50.27	49.04	1.23	884.45	2.45
77.79	77.02	0.77	853.45	0.99
45.76	44.64	1.12	898.87	2.45
71.62	70.90	0.72	850.73	1.01
61.52	60.00	1.52	882.78	2.47
79.65	78.89	0.76	843.82	0.95
47.39	46.42	0.97	859.09	2.05
71.53	70.82	0.72	844.85	1.00
55.05	53.93	1.12	890.32	2.03
76.27	75.95	0.32	823.13	0.42
45.96	45.06	0.90	861.96	1.96
79.62	79.30	0.32	803.06	0.40
57.14	55.99	1.15	869.58	2.01
75.53	75.25	0.28	830.73	0.37
51.97	50.93	1.04	862.16	2.00
71.58	71.32	0.26	831.70	0.36
46.89	45.95	0.94	864.13	2.00
73.32	73.00	0.32	820.46	0.44
53.50	52.43	1.07	868.88	2.00
68.97	68.56	0.41	829.19	0.59
52.26	51.27	0.99	862.28	1.89
70.55	70.29	0.26	829.78	0.37
51.97	50.99	0.98	868.93	1.89
65.46	65.13	0.33	832.72	0.50
50.75	49.79	0.96	886.77	1.89
73.97	73.66	0.31	828.10	0.42
53.01	51.99	1.02	863.86	1.92
59.03	57.88	1.15	889.67	1.95
72.66	71.67	0.99	852.91	1.36
55.29	54.54	0.75	864.41	1.36
56.70	55.94	0.76	860.87	1.34
65.37	64.49	0.88	858.90	1.35
61.55	0.73	0.82	851.41	1.33

Note: The enthalpy measurements were made on drops from 22 to 784 °C and are reported on an anhydrous cordierite basis.

with a standard error in the determination of the enthalpy of 8.193 J/g-Crd. By using Equation 5, the enthalpy of Reaction 2 with $n = 1$ (or 0.030 797 3 g-H_2O/g-Crd) is 932.121 ± 8.193 J/g-Crd. A revised value of the enthalpy of Reaction 3 is obtained in the linear regression of −811.979 ± 1.142 J/g-Crd, which is essentially identical to that measured for anhydrous cordierite alone (−811.604).

Enthalpy of dehydration

Table 5. Data on the thermochemical cycle for $nH_2O = 1$

Reaction	J/g-Crd	J/mol
2	932.121 ± 8.193	545 247 ± 4793
3	−811.979 ± 1.142	−474 969 ± 668
4	−48.665	−28467
1 = 2 + 3 + 4	71.477 ± 2.711	41811 ± 1586

Note: Molar weight of anhydrous cordierite = 584.953 g/mol and H_2O = 18.015 g/mol. The indicated uncertainties are standard errors derived from linear regression of the enthalpy measurements.

Calculations for the entire thermochemical cycle are summarized in Table 5. The molar enthalpy of dehydration, Reaction 1 with $n = 1$, is 71.477 ± 2.711 J/g-Crd. The standard error of the measurement is equivalent to the standard error of the slope of Equation 5 translated from J/g-H_2O to J/g-Crd and with any uncertainty in the data ignored for pure H_2O. This is an appropriate estimate of the error because the sum of Reactions 2 and 3 with $n = 1$ is equivalent to the slope. Translated from a mass to a mole basis, the molar enthalpy of dehydration is 41811 ± 1586 J/mol with $n = 1$ at the reference conditions 22 °C, 1 bar, and gaseous H_2O. At the 95% confidence level with the Student's *t* test with 91 degrees of freedom, the molar enthalpy of dehydration of hydrous cordierite lies between 38661 and 44961 J/mol.

DISCUSSION

Enthalpy of mixing and the maximum H_2O content of cordierite

The linear trend of the data in Figure 2 indicates a constant partial molar enthalpy of dehydration equal to the molar value. Consequently, the enthalpy of mixing of H_2O in magnesium cordierite is equal to zero over the investigated range from $n = 0$ to $n = 0.84$. This result is consistent with a site occupancy of a single H_2O molecule per cage because the energetic effect of double occupancy would be reflected in a positive enthalpy of mixing.

The data suggest a thermodynamic formulation for hydrous cordierite with an ideal enthalpy of mixing based upon a maximum H_2O content of $n = 1$. Such a formulation would not be able to account for some of the synthesis data of Mirwald et al. (1979) and several analyses of natural cordierite summarized by Leake (1960) in which $n > 1$ and double occupancy of the cages is indicated. However, the synthesis conditions that produced values of $n > 1$ are outside of the stability field of magnesium cordierite and are probably not relevant to natural cordierite. It is also possible that the excess H_2O in samples used by Mirwald et al. is located along grain boundaries, fluid inclusions, or undetected phyllosilicates. The natural samples may also have been contaminated by undetected phyllosilicates or fluid inclusions, but the data are difficult to evaluate. In summary, all of the syntheses that lie within cordierite's stability field, the large majority of analyses of natural cordierite, and the results of this study on the enthalpy of mixing in hydrous cordierite indicate that the most effective thermodynamic formulation for hydrous cordierite is one based upon a maximum H_2O content of $n = 1$.

TABLE 6. Comparative enthalpies of dehydration at 25 °C

System	$\Delta H_{\mathrm{dehyd}}$ (kJ/mol)	Comments
H_2O	40.9	enthalpy of vaporization*
Cordierite	41.8	this study
Analcime	84.9	HF solution calorimetry**
Mordenite	73.8	HF solution calorimetry†
Clinoptilolite	67.4	HF solution calorimetry‡
Sodium mordenite	70.3	reaction calorimetry§
Hydrogen mordenite	58.7	reaction calorimetry§
Sodium clinoptilolite	66.1	reaction calorimetry§
Hydrogen clinoptilolite	55.6	reaction calorimetry§
Sodium chabazite	70.0	reaction calorimetry§
Sodium ferrierite	61.3	reaction calorimetry§
Na-X	68.7	reaction calorimetry§
Na-Y	61.6	reaction calorimetry§
Na-A	69.9	reaction calorimetry§

* Robie et al. (1978).
** Johnson et al. (1982).
† Johnson et al. (1986).
‡ Johnson et al. (1991).
§ Barrer and Cram (1971).

Enthalpy of dehydration at 25 °C and the enthalpy of formation

The molar enthalpy of dehydration of cordierite may be adjusted to a standard state of 25 °C, 1 bar, using the results of heat-capacity measurements of hydrous cordierite presented by Carey (1990a, 1990b). The net heat capacity of dehydration (Reaction 1) for $n = 1$ is -9.72 $J/mol \cdot H_2O/°C$ at 25 °C. This value is essentially constant over the interval of 3 °C from 22 to 25 °C, yielding a standard-state molar enthalpy of dehydration of 41782 J/mol.

The enthalpy of formation of hydrous cordierite may be calculated from the enthalpy of dehydration data in combination with data in Robie et al. (1978) according to the following relation:

$$\Delta H_f\,(\mathrm{Crd}\cdot H_2O) = \Delta H_f\,(\mathrm{Crd}) + \Delta H_f\,(H_2O) + \Delta H\,(\mathrm{hydration}). \qquad (6)$$

The result is -9445.120 ± 1.586 kJ/mol from the elements at 25 °C and 1 bar or -95.426 kJ/mol from the oxides.

Comparison with data derived from phase equilibria

Previous estimates of the molar enthalpy of dehydration have been derived from synthesis experiments of hydrous cordierite, principally those of Schreyer and Yoder (1964) and Mirwald et al. (1979), and phase-equilibrium experiments involving hydrous cordierite. These estimates required various assumptions or inferences to be made concerning the heat capacity of hydrous cordierite, the number of crystallographic sites for H_2O, the molar volume of hydrous cordierite, and the nature of mixing of H_2O in cordierite. Despite these approximations, the estimates have provided reasonable values both greater than and less than the calorimetrically determined value: Helgeson et al. (1978), 34.4 kJ/mol; Newton and Wood (1979), 42.9 kJ/mol; Lonker (1981), 32.3–45.8 kJ/mol; Bhattacharya and Sen (1985), 29.2 kJ/mol; and McPhail et al. (1990), 38.5 kJ/mol. The successful predictions imply that the synthesis experiments yield reasonable approximations to the equilibrium properties of the cordierite-H_2O system. Since all of the thermodynamic models assume ideal mixing, the entropy as well as the enthalpy of cordierite-H_2O solutions appears to behave ideally.

Comparison to H_2O and zeolites

The molar enthalpy of dehydration of cordierite is the same as the molar enthalpy of vaporization of water within experimental uncertainty (Table 6). The difference (916 J/mol) is within the standard error of the measurements. In fact, if the standard state of H_2O is taken as liquid at 25 °C, the enthalpy of dewatering is marginally exothermic: -2234 ± 1536 J/mol. These results indicate that the molecular environment of H_2O in cordierite is similar to that of H_2O in water. In both cases, the H_2O is held by some form of H bonding.

Zeolites, in contrast, have molar enthalpies of dehydration 10–40 kJ/mol in excess of cordierite or of the molar enthalpy of vaporization of water (Table 6). They range from a high of 84.9 kJ/mol for analcime to a low of 61.3 kJ/mol for sodium ferrierite. Also listed in Table 6 are molar enthalpies of dehydration for decationated and dealuminated mordenite and clinoptilolite that have reduced values of 58.7 and 55.6 kJ/mol, respectively. Barrer and Cram (1971) modified these zeolites by treatment in a strong acid that replaces Al cations with OH groups. These defect structures have neutral frameworks that do not require charge-balancing cations in the cage (in the case of clinoptilolite) or have 25% of the original cation content (in the case of mordenite). The reduced molar enthalpies of dehydration demonstrate the important energetic role played by the cations in the zeolite cages.

The partial molar enthalpy of dehydration in zeolites, in contrast to that in cordierite, is strongly dependent on H_2O content (Barrer and Fender, 1961; Barrer and Denny, 1964; Barrer and Cram, 1971; Dzhigit et al., 1971). In Na-X and Na-A, for example, the partial molar enthalpy of dehydration increases from 46 kJ/mol at the onset of dehydration to 63 kJ/mol at 24% of dehydration (Barrer and Denny, 1964). Similarly, Barrer and Cram (1971) found that a calcium sodium chabazite sample was characterized by initial partial molar enthalpies of dehydration of 71 kJ/mol and final values near 117 kJ/mol. The enthalpy of mixing of H_2O in most zeolites is nonideal.

These observations suggest that the behavior of zeolite-type systems consist of two energetically distinct processes (e.g., Barrer, 1978). The adsorption of H_2O involves both the filling of O-lined cages and the solvation of any cations present in the cages. The energetics of the cage-filling process are exemplified by the enthalpy of dehydration of cordierite or the enthalpy of vaporization of water. The energetics of the solvation of cations may be seen in the work of Barrer and Cram (1971) on decationated and dealuminated zeolites or in the relationship depicted in Figure 3. This diagram shows the enthalpy of dehydration as a function of the ratio of the number of cations to H_2O molecules for a variety of sodium zeolites. As this ratio increases, the percentage of H_2O molecules involved in the first coordination or solvation of the cations increases. This limited data set is not linear but does show a monotonic increase in the enthalpy of dehydration as the relative number of H_2O molecules decreases.

This twofold view of the adsorption process also accounts for the nonideal enthalpy of mixing of H_2O in zeolites. The initial stages of dehydration may be characterized by the loss of H_2O molecules not involved in the solvation of cations and therefore having a partial molar enthalpy of dehydration closer in value to that of cordierite. As the dehydration process continues, H_2O molecules more closely involved in the solvation of the cations are removed, with a corresponding increase in the partial molar enthalpy of dehydration.

Application of results to natural cordierite compositions

The principal chemical and structural differences that may be found in natural cordierite compared to the synthetic magnesium cordierite used in these experiments are the possible existence of Al-Si disorder, the presence of Fe^{2+} in the octahedral sites, and the occurrence of alkali cations in the ring necks of the H_2O-bearing cages. Neither Al-Si disorder nor Fe^{2+} are likely to have a first-order effect on the molar enthalpy of dehydration, as these are isolated from the H_2O molecules by the O ions lining the cages. There has been no systematic work on Al-Si disorder that bears on this issue. Boberski and Schreyer (1990) synthesized hydrous iron cordierite and obtained hydration states similar to those in magnesium cordierite, which is consistent with similar enthalpies of dehydration for the Mg and Fe end-members.

Alkali cations in cordierite channels are likely to have a first-order effect on the enthalpies of dehydration. An estimate of the magnitude of this effect may be obtained from the relationship in Figure 3. The maximum Na content observed in natural cordierite is 0.42 per formula unit (Gordillo et al., 1985). Using 0.5 Na and 1.0 H_2O per formula unit, the data on zeolites suggest that the molar enthalpy of dehydration could increase to as much as 70 kJ/mol for this composition.

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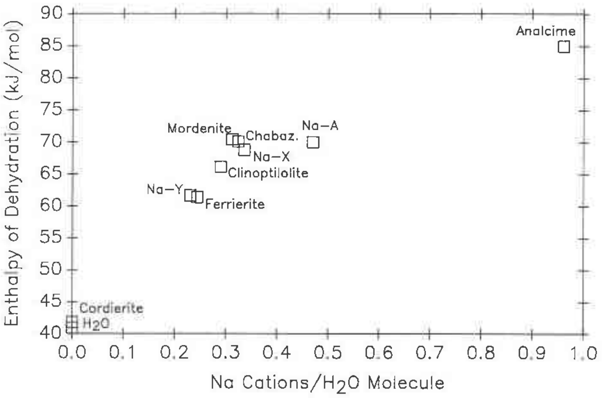

Fig. 3. The molar enthalpy of dehydration of cordierite, several Na-bearing zeolites, and the molar enthalpy of vaporization of water. The data are plotted as a function of the ratio of Na cations (or framework charge) to H_2O molecules.

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