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The free energy of formation of datolite

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ABSTRACT

The solubility of datolite, $CaBSiO_4(OH)$, has been determined experimentally at temperatures from 100 to 250 °C and $P_V = P_{H_2O}$. Activity products (Q) were calculated for the dissolution reaction after 8–10 time intervals in experiments of up to four months' duration in order to determine K_{eq}. A linear relationship between log K_{eq} and reciprocal temperature [$\log K_{eq} = 4.405 + 637.0/T$ (K); $R = 0.97$] suggests the attainment of equilibrium. The ΔG_f^0 extrapolated to 25 °C, −2318 ± 2 kJ/mol, is the same as a calculated calorimetric value (Semenov et al., 1988) and close to the value of −2317 kJ/mol estimated with the use of the polyhedral model of Chermak and Rimstidt (1989). However, at elevated temperatures ΔG_f^0 values determined from solubility data diverge from the other two estimations, suggesting that the latter may be more accurate.

The ΔG_f^0 values calculated from the data of Semenov et al. (1988) have been used to determine the temperature dependence of datolite-danburite stability relations and activity diagrams for the system CaO-B_2O_3-SiO_2-H_2O at 250 °C in an effort to place limits on solution compositions in equilibrium with mineral assemblages in the quaternary system. Higher activities of $H_3BO_{3,aq}$ and $SiO_{2,aq}$ and lower pH are required for the formation of danburite than for datolite, whereas high $a_{Ca^{2+}}$ favors the crystallization of datolite.

INTRODUCTION

Although calcium borosilicates are not rare minerals, few mineralogical, field, or laboratory studies have sought to account for their genesis. Thus, qualitative statements concerning the chemistry of fluids responsible for the crystallization of datolite or danburite are the rule (e.g. Eugster and Wise, 1963). For example, the higher CaO/B_2O_3 ratio in datolite than danburite must reflect the compositions of the fluids that coexisted with these minerals, but what are these compositions and how do they vary with temperature and pressure? While some experimental and calorimetric data are available (Kurshakova, 1982; Semenov et al., 1988), much more are necessary to define the stability relations of calcium borosilicates in the system CaO-B_2O_3-SiO_2-H_2O. The present investigation is a contribution to this effort.

B-bearing minerals have not, as yet, been included in internally consistent, thermodynamic data sets (e.g., Berman, 1988; Holland and Powell, 1990) largely because of the paucity of data currently available for these minerals. Few reactions involving borosilicates have been studied experimentally and published calorimetric studies are incomplete. However, efforts are now underway to fill this information gap, particularly for the calcium borosilicates, danburite, $CaB_2Si_2O_8$, and datolite, $CaBSiO_4(OH)$, which occur in a wide variety of geologic environments. When these data are available, the calculation of the stability relationships of the calcium borosilicates in solutions of varying composition will be possible over a wide temperature range. A knowledge of these phase relations would be of interest in studies of water/rock interactions in B-bearing systems.

The stability relations of danburite and datolite were determined experimentally by Eugster and Wise (1963) and more recently by Kurshakova (1982), but thermodynamic data was not retrieved. The enthalpy of formation (ΔH_f^0) of danburite was determined calorimetrically by Semenov et al. (1988); earlier entropy, and specific heat measurements for datolite and danburite (Zhdanov et al., 1977; Agoshkov et al., 1977) were also tabulated. The standard enthalpy of formation of datolite was then calculated using P-T data for the reaction

$$2CaBSiO_4(OH) + SiO_2 = CaB_2Si_2O_8 + CaSiO_3 + H_2O \quad (1)$$

(Eugster and Wise, 1963) and thermodynamic data from the literature; the free energy of formation of datolite calculated from the data published by Semenov et al. (1988) is −2318 ± 2 kJ/mol.

More recently, heat capacity data for danburite and datolite have become available (Mazdab et al., 1992), but the enthalpy of formation of datolite and, thus, its free energy of formation have never been determined directly. The standard entropy and heat capacity of danburite quoted by Semenov et al. (1988), 154.8 ± 2.1 J/(mol·K) and 185.1 ± 0.9 J/(mol·K), respectively, are in close agreement with the values determined by Mazdab et al. (1992) [$S^0 = 155.4$ J/(mol·K), $C_P^0 = 185.0$ J/(mol·K); the

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S^0_{298} value given for danburite by Mazdab et al. (1992) is actually their value for $C^0_{P,298}$; L. M. Anovitz, personal communication]. Measured values of $H^0_{973.15}$ for danburite are also nearly identical (186.1 kJ/mol: Semenov et al., 1988; 185.2 kJ/mol: L. M. Anovitz, personal communication). These studies provide a reliable database for danburite, but the thermochemical parameters of datolite are less well known. In order to provide direct measurements for datolite, a solubility study was undertaken in the temperature range 100–250 °C.

Datolite is stable with respect to danburite in the system CaO-B_2O_3-SiO_2-H_2O at low temperatures and H_3BO_3 activities. At low temperatures (<200 °C) datolite reacts to form $CaB_6O_9(OH)_2 \cdot H_2O$ + quartz (Kurshakova, 1982). Although the lower thermal stability limit has not been firmly established, extrapolation of the experimental data of Kurshakova (1982) suggests that, at the extremely low activities of H_3BO_3 anticipated in solubility studies, datolite may be stable above about 125 °C. Preliminary experiments in this laboratory show, however, that datolite persists up to four months at 100 °C; reaction products were not detected by X-ray diffractometry or by optical and electron microscopy. Alteration products (calcium borates) have been recently observed under the electron microscope in the products of long-term experiments at lower temperatures (Yang, 1990). Thus, datolite appears to be suitable for solubility studies above 100 °C but not below this temperature.

SOLUBILITY STUDIES

Starting materials

Datolite from Summit, New Jersey (Wards research-grade), occurs in fine-grained (<0.2 mm diameter) aggregates with calcite and minor amounts of quartz. The bulk sample was ground to <50 μm. To remove the carbonate, the sample was washed with a dilute sodium acetate solution following the procedures of Kittrick and Hope (1963). Quartz was not separated because it does not significantly affect the solubility of datolite under the experimental conditions of this study (silica concentrations in the experiments were higher than those for quartz equilibrium). Preliminary experiments suggested that some amorphous silica may be present in the sample; it was removed by washing with 0.5*N* NaOH solution (Foster, 1953) followed by rinsing with double distilled water. The size fraction <0.2 μm was discarded and the remaining mineral powder was dried at 60 °C. Double distilled water was used as the starting solution in all experiments.

Laboratory procedures

All experiments were carried out in Teflon(PTFE)-lined, Al or stainless steel pressure vessels. The 20 mL Teflon liners contained 12–15 mL H_2O and 0.5–2 g of mineral powder. These vessels were heated in ovens for up to four months and then quenched to room temperature in 5–15 min in cold water (Sass et al., 1987; Aja, 1989). The time required for quenching the Al vessels was generally shorter than that for the stainless steel vessels.

TABLE 1. Analytical data (EPMA*) for datolite and its ideal composition (in weight percent)

	Datolite	
Oxide	EPMA	Ideal
Na_2O	0.02	0.00
FeO	0.03	0.00
K_2O	0.00	0.00
SiO_2	36.56	37.56
CaO	34.39	35.05
Al_2O_3	0.01	0.00
TiO_2	0.03	0.00
MgO	0.01	0.00
MnO	0.02	0.00
B_2O_3	—	21.76
H_2O	—	5.63
Total	71.01	100.00

* Average of six point analyses.

After quenching, solutions were filtered through 0.1 μm filters in <5 min; pH was measured immediately after filtration. Solutions were diluted for analysis immediately after filtration to prevent precipitation due to decreasing temperature. SiO_2 and B concentrations in the solutions were determined within 5 h, whereas Ca was analyzed within 24 h after the termination of an experiment. Solid materials were washed in a centrifuge using distilled water and dried at 60 °C for examination by X-ray diffractometry and optical microscopy.

Analytical methods

Solid products were characterized by X-ray powder diffractometry and optical microscopy. The chemical composition of the datolite samples was determined by electron microprobe analysis (Table 1). Inasmuch as insignificant amounts of nonessential elements were observed, the ideal formula has been used throughout this study; elements present in datolite at low concentrations (eg., Fe, Ti) were not determined in the dissolution experiments.

The colorimetric, azomethine-H method (John et al., 1975) was used to determine B concentrations in solution with an error of <3%. Aqueous silica was analyzed using the molybdosilicate method (Skougstad et al., 1979) with an estimated precision of ±5%. Ca concentrations were determined to within 10% by atomic absorption spectrophotometry (AA). The pH values were measured at room temperature with a precision of ±0.05 pH units using a combination glass electrode and a Beckman 71 pH meter standardized with two buffers. The overall error in the free energy of formation of datolite, owing to analytical uncertainties, is estimated to be <2 kJ/mol.

Calculations

Activity coefficients and pH at elevated temperatures were calculated from concentrations and pH measured at 25 °C and with the use of the program SOLVEQ (Reed, 1981) by adding stability data for the B species to the database (compiled in Yang and Rosenberg, 1992, Table 1). At a total B concentration $<0.01M$, $H_3BO_3^0$ and

TABLE 2. The ΔG_f^0 values of the aqueous species at 100–250 °C

T (°C)	SiO_2^0 (kJ/mol)	$H_3BO_3^0$ (kJ/mol)	H_2O (kJ/mol)	Ca^{2+} (kJ/mol)
100	−837.64	−980.86	−243.09	−548.27
150	−840.48	−989.39	−247.66	−544.92
200	−843.62	−998.26	−252.68	−541.12
250	−846.97	−1007.55	−258.10	−536.81

Note: calculated with SUPCRT92 (Johnson et al., 1992).

TABLE 3. Results of datolite dissolution experiments (calculated from data in Appendix Table 1)

T (°C)	$pH_3BO_3^0$	$pSiO_2$	pCa	pH	log K	ΔG_f^0	t (d)
100	2.93	2.29	3.09	7.21	6.10	−2323.16	123
150	2.25	1.96	3.38	6.75	5.91	−2326.90	141
200	2.43	2.20	3.47	6.97	5.83	−2330.16	82
250	1.71	1.90	3.32	6.28	5.64	−2334.81	98

$B(OH)_4^-$ are the only significant species in solution; they equilibrate according to the reaction $B(OH)_4^- + H^+ = H_3BO_3^0 + H_2O$.

At 25 °C, log K for this reaction is 9.24 (Mesmer et al., 1972) and thus, the activities of $H_3BO_3^0$ and $B(OH)_4^-$ are equal when pH = 9.24. At lower pH values, $H_3BO_3^0$ is the major species in solution, whereas at higher pH values $B(OH)_4^-$ predominates.

The stability constant of $CaB(OH)_4^+$, the only other species of importance in these solutions, was linearly extrapolated from values between 10 and 50 °C (Reardon, 1976). Because the concentrations of B (>30 mmol/L) and Ca (<1 mmol/L) in solution are quite low (Yang, 1990), the error caused by extrapolation from data at lower temperatures is assumed to be small.

Free energies of formation were calculated with the use of the standard-state convention of Helgeson et al. (1978) because the thermodynamic data for aqueous species used in this study (SPUCRT92: Johnson et al. 1992) are based on this convention. The free energies of formation (ΔG_f^0) of the aqueous species used in this study are listed in Table 2.

The dissolution reaction for datolite is given by the equation

$$CaBSiO_4(OH) + 2H^+ = Ca^{2+} + H_3BO_{3,aq} + SiO_{2,aq}. \quad (2)$$

The equilibrium constant, K_2, for Reaction 2 can be calculated using the equation

$$\log K_2 = \log a_{Ca^{2+}} + \log a_{H_3BO_3} + \log a_{SiO_{2,aq}} - 2 \log a_{H^+} \quad (3)$$

where a denotes the activity of the chemical species when the reaction is at equilibrium. The free energy of reaction ΔG_r^0, can then be calculated from the log K_2 value using the relationship

$$\Delta G_r^0 = -2.303RT \log K_2 \quad (4)$$

where R refers to the gas constant and T represents the temperature in Kelvins. Because the ΔG_f^0 of the species in solution are known (Table 2), $\Delta G_{f,datolite}^0$ can be calculated by difference from the equation

$$\Delta G_{f,datolite} = \Delta G_{f,Ca^{2+}}^0 + \Delta G_{f,H_3BO_3}^0 + \Delta G_{f,SiO_{2,aq}}^0 - 2\Delta G_{f,H^+}^0 - \Delta G_r^0. \quad (5)$$

Experimental results

Solution compositions after the experiments are compiled in Appendix Table 1. The calculated activities of chemical species, log K values, and free energies of formation of datolite are listed in Table 3.

The activity product, Q_2, for the datolite dissolution reaction (Eq. 2) is given by the equation

$$\log Q_2 = \log a_{Ca^{2+}} + \log a_{H_3BO_3} + \log a_{SiO_{2,aq}} - 2 \log a_{H^+} \quad (6)$$

where a represents the activities of the chemical species in solution. As the dissolution reaction progresses, log Q_2 converges toward a limiting value. When the system reaches equilibrium, log Q_2 = log K_2(Eq. 3), where K is the equilibrium constant.

The results of the experiments are summarized in Table 4. Values of log Q obtained in experiments of about 20 d duration were essentially unchanged in experiments of much longer durations ranging up to 141 d at 150 °C (Appendix Table 1). Experiments using supersaturated starting solutions were also attempted, generally without success. However, one such experiment at 250 °C (Appendix Table 1, DT25) appears to have approached equilibrium. Calculated log K values and free energies of formation are given in Table 4.

The variation of log K with 1000/T (K) approximates a straight line (Fig. 1), which can be described by the equation $\log K = 4.4046 + 637.04/T$ (K) ($R = 0.97$). The linear relationship suggests that equilibrium was probably attained and that ΔH_r^0 for the dissolution of datolite is approximately constant over the temperature range of this study.

Semenov et al. (1988) published measured ΔH_f^0 and S^0 values for danburite at 25 °C. The ΔG_f^0 of datolite, calculated from their data using Reaction 1 is −2318 ± 2 kJ/mol, which is the same as the value obtained in this study by extrapolation of high temperature data to 25 °C (Fig. 1; Table 4). Inasmuch as the thermodynamic parameters of the other phases in Reaction 1 are quite well known, the experimental confirmation of the free energy of formation of datolite implies that the entropy and enthalpy (ΔH_f^0) values given by Semenov et al. (1988) are essentially correct. However, at temperatures above 25 °C, values of ΔG_f^0 calculated from data given by Semenov et al. (1988) diverge from those measured in the present study (Table 5). Thermodynamic parameters for datolite have been estimated for purposes of comparison, in an attempt to resolve this discrepancy.

ESTIMATION OF THERMODYNAMIC DATA

Although the available methods for estimation of thermodynamic properties of minerals are not fully satisfac

Table 4. The average values of the equilibrium constant (log *K*) for the datolite dissolution reaction and the free energy of formation of datolite at 25–250 °C

T (°C)	log *K*	ΔG_f^0 (kJ/mol)
25	6.54*	−2318
50	6.38*	−2320
100	6.10	−2323
150	5.91	−2327
200	5.83	−2330
250	5.64	−2335

* Extrapolated from experimental data at higher temperatures.

tory at present, they do provide a basis for comparison with experimentally determined values. The most promising of these methods, both in its apparent ability to estimate thermodynamic properties at present and in its potential for future development, is based on the polyhedral model (Chermak and Rimstidt, 1989, 1990; Holland, 1989; Robinson and Haas, 1983).

Chermak and Rimstidt (1989) proposed a method for the estimation of the ΔH_f^0 and ΔG_f^0 of silicates at 25 °C on the basis of the sums of the polyhedral-unit contributions. Donahoe et al. (1990) used this method to calculate the free energies of formation of six merlinoite samples to within 0.16% of the experimental values, but the average accuracy is probably about 0.26% (Aja et al., 1992). Earlier, Robinson and Haas (1983) estimated heat capacities and entropies of some minerals to within 2% and Holland (1989) improved the entropy estimates by introducing a molar-volume term, but deviations from known values were still considered to be unsatisfactory for some minerals.

Because of the limitations of the polyhedral model in its present form, Aja et al. (1992) proposed refinements that would significantly improve the accuracy of estimates of these thermochemical variables. However, a revised model would require additional data, which are not available, as yet, for most minerals. Therefore, estimates based on the original polyhedral model of Chermak and Rimstidt (1989) have been made for purposes of comparison with the somewhat discordant ΔG_f^0 values of Semenov et al. (1988) and this study (Table 5).

Estimated free energy of formation

The polyhedral model of Chermak and Rimstidt (1989) as modified by Holland (1989) has been used to estimate ΔH_f^0 and S^0, respectively; ΔG_f^0 has been calculated at 25 °C using these values. The ΔG_f^0 values at high temperatures have been calculated by extrapolating the value at 25 °C using estimated C_P functions (Robinson and Haas, 1983). Thermodynamic data for danburite (Semenov et al., 1988) have been used throughout to calculate the fictive properties of B_2O_3 with B in tetrahedral coordination.

Estimation of entropy

Using the procedure of Holland (1989), the entropy of danburite (S^0) can be calculated as

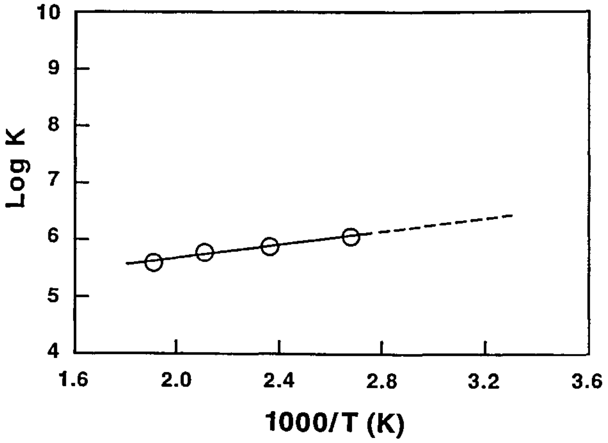

Fig. 1. Variation of the equilibrium constant (*K*) with reciprocal temperature (*T*). The straight line [$\log K = 4.4046 + 637.04/T$ (K); $R = 0.97$] is based on linear regression analysis of the data (circles). Symbol size is approximately equal to analytical error. Datolite is metastable below 100 °C (dashed extension).

$$S^0_{\text{danburite}} = V^0_{\text{danburite}} + 0.5S'({}^{[6]}\text{CaO}) + 0.5S'({}^{[8]}\text{CaO}) + S'({}^{[4]}\text{B}_2\text{O}_3) + 2S'({}^{[4]}\text{SiO}_2) \qquad (7)$$

where V^0 is the molar volume. The superscripts (numbers in brackets) denote the coordinations of the cations. Both $S'({}^{[6]}\text{CaO})$ and $S'({}^{[8]}\text{CaO})$ appear in equation 7 (and in the calculations of other fictive properties) because in danburite Ca is in sevenfold coordination (Johansson, 1959), which is not included in the Holland (1989) model. It is assumed that by averaging values for sixfold and eightfold coordination, a reasonable estimate of the value for sevenfold coordination is obtained.

Using the S' values for CaO and SiO_2 given by Holland (1989) and the S^0 value of danburite [154.8 J/(mol·K)] given by Semenov et al. (1988), $S'({}^{[4]}\text{B}_2\text{O}_3)$ is calculated as 13.17 J/(mol·K) from Equation 7.

V^0 of datolite (53.4 cm³/mol) was calculated from the density data in Erd (1980). The estimated entropy of datolite [112.6 J/(mol·K)] is close to the experimental value [110.0 J/(mol·K): Semenov et al., 1988]. The difference is only 2.4%, which is small compared to the 5–15% differences observed with other commonly used entropy estimation methods (Holland, 1989).

Table 5. Estimated and measured free energies of formation of datolite at 25, 50, 100, 150, 200, and 250 °C (kJ/mol)

T (°C)	Estimated	Semenov et al., 1988	This study
25	−2316.9	−2318.4	−2317.7
50	−2319.9	−2321.3	−2319.5
100	−2326.5	−2327.8	−2323.2
150	−2334.2	−2335.4	−2326.9
200	−2342.8	−2343.9	−2330.2
250	−2352.3	−2353.2	−2334.8

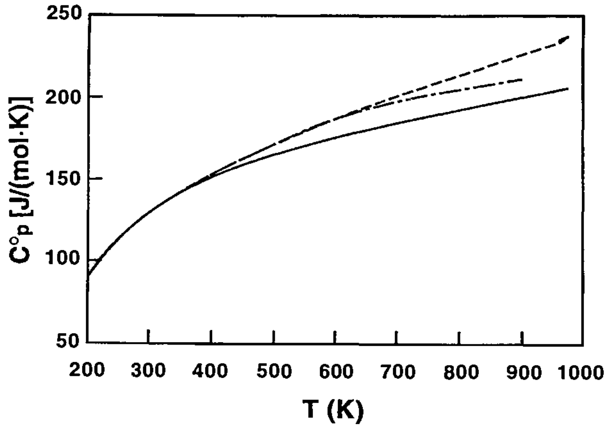

Fig. 2. Estimated and measured heat capacity functions (C°_P) of datolite. Solid line, Semenov et al. (1988); dash-dot line, Mazdab et al. (1992); dashed line, estimated values, this study.

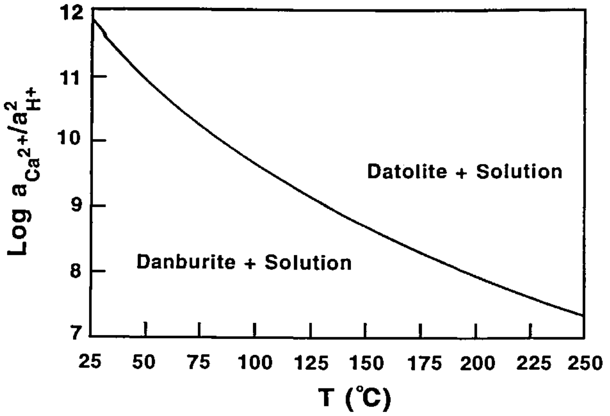

Fig. 3. Variation of the equilibrium constant (log $a_{Ca^{2+}}/a^2_{H^+}$) with temperature for the reaction, $2CaBSiO_4(OH)$ (datolite) + $2H^+$ = $CaB_2Si_2O_8$ (danburite) + Ca^{2+} + $2H_2O$. Datolite metastable below 100 °C.

Estimation of enthalpy and free energy of formation

Using the method of Chermak and Rimstidt (1989) the fictive enthalpy of formation of danburite may be estimated with the equation,

$$H^\circ_{f,\mathrm{danburite}} = 0.5h({}^{[6]}CaO) + 0.5h({}^{[8]}CaO) + h({}^{[4]}B_2O_3) + 2h({}^{[4]}SiO_2). \quad (8)$$

Using the h values of the other oxides, determined by Chermak and Rimstidt (1989) and $\Delta H^\circ_{f,\mathrm{danburite}}$ (Semenov et al., 1988), $h({}^{[4]}B_2O_3)$, calculated from Equation 8, is -1364.52 kJ/mol.

The free energies of formation of danburite and datolite are calculated using the equation

$$\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f \quad (9)$$

where T is the temperature in Kelvins and ΔH°_f is the estimated enthalpy of formation. The ΔS°_f is the entropy of formation, which was calculated from the estimated S° of the mineral and the third law entropies of the elements (Robie et al., 1978).

The estimated ΔH°_f and ΔG°_f values of datolite, -2476 and -2317 kJ/mol, respectively, are essentially the same as the values, -2478 and -2318 kJ/mol, calculated by Semenov et al. (1988). The free energy of formation of datolite extrapolated from data at higher temperatures, -2318 kJ/mol, in the present investigation is in close agreement with both of the above values.

Estimation of heat capacity functions

The fictive heat capacity function of ${}^{[4]}B_2O_3$ has been calculated from the measured heat capacity of danburite (Zhdanov et al., 1977; Agoshkov et al., 1977) and its other component oxides (Robinson and Haas, 1983). The fictive heat capacity function of ${}^{[4]}B_2O_3$ is calculated using the equation

$$C'_{P^{[4]}B_2O_3} = a + 2bT + cT^{-2} + fT^2 + gT^{-0.5} \quad (10)$$

where T is temperature in Kelvins and the fictive heat capacity functions are estimated as the following: $a = -1.68430 \times 10^2$; $b = 12.1640 \times 10^{-2}$; $c = -2.64176 \times 10^6$; $f = 0.00000 \times 10^{-5}$; $g = 3.06000 \times 10^3$. The heat capacity function of ${}^{[4]}B_2O_3$ was then used to calculate the temperature dependence of the heat capacity of datolite following the procedure of Robinson and Haas (1983). The estimated heat capacity function is

$$C_P = \Sigma N_i C_{P,i} = 1.7334 \times 10^2 + 2(5.2059 \times 10^{-2})T + (-9.8518 \times 10^5)T^{-2} + (0.0000)T^2 + (-1.0921 \times 10^3)T^{-0.5} \quad (11)$$

where N_i is the stoichiometric coefficient of the ith component and $A = \Sigma N_i a_i$, $B = \Sigma N_i b_i$, etc.; the lower case letters are coefficients obtained by multiple regression analysis of a large number of minerals (Robinson and Haas, 1983).

A comparison of the experimental and estimated heat capacity functions is shown in Figure 2. At temperatures below 500 K, the three C°_P vs. temperature curves are essentially coincident. However, the Semenov et al. (1988) and Mazdab et al. (1992) functions diverge from the estimated curve above 400 and 650 K, respectively, the differences becoming larger at higher temperatures. At 973.15 K (700 °C), the difference between the estimated heat capacity and the value predicted by Semenov et al. (1988) is about 30 J/(mol·K) (14%). However, this results in a difference in ΔG°_f of only 3 kJ/mol, which is about 0.1% of the ΔG°_f of datolite at 700 °C. Considering that the estimation of ΔG°_f at 25 °C has an error of 0.34%, the error caused by the estimation of heat capacities is not significant. At temperatures below 250 °C, the ΔG°_f calculated using the estimated heat capacity is identical to that calculated with the experimental heat capacity. Therefore, the procedure for heat capacity estimation of Robinson and Haas (1983) appears to be applicable to borosilicates with B in tetrahedral coordination.

Thermodynamic properties at higher temperatures

Inasmuch as the S^0, ΔH_f^0, ΔG_f^0 (at 25 °C), and the heat capacity functions of datolite have been estimated, its thermodynamic properties at higher temperatures can be calculated. As an overall test of the estimation procedures, the estimated ΔG_f^0 of datolite at elevated temperatures have been estimated and compared with experimentally determined values (Table 5). The estimated free energy values of datolite at elevated temperatures were calculated from the estimated ΔG_f^0 at 25 °C (Table 5), the estimated S^0 at 25 °C, and the estimated C_P functions. The maximum difference between the estimated free energies and the free energies of Semenov et al. (1988) is 1.4 kJ/mol (Table 5). Because the uncertainty in the values of Semenov et al. (1988) is ±2.9 kJ/mol, the estimated free energies are within the limits of error of the Semenov et al. (1988) values. At temperatures below 100 °C, the extrapolated values determined in this study also closely approximate the estimated free energies, but they diverge at higher temperatures; at 250 °C the difference is about 0.7%.

DISCUSSION

Inasmuch as the estimated ΔG_f^0 value and both of the measured ΔG_f^0 values agree within <0.1% at 25 °C, the free energy of formation of datolite is probably known with sufficient accuracy to permit calculation of phase relationships in the system CaO-B_2O_3-SiO_2-H_2O. However, datolite appears to be metastable at temperatures below about 100 °C at low activities of H_3BO_3 (Kurshakova, 1982; Yang, 1990).

Comparison of the ΔG_f^0 values at the higher temperatures (Table 5), at which datolite and danburite are stable in the presence of H_3BO_3-bearing solutions (Kurshakova, 1982), might suggest that the thermodynamic properties of the calcium borosilicates are not known with sufficient accuracy to permit the construction of meaningful phase diagrams. However, the Semenov et al. (1988) free energies are <0.1% more negative than the estimated values over the entire temperature range from 25 to 250 °C (Table 5); at 250 °C the difference is only 0.04%. Although the ΔG_f^0 values based on the solubility studies reported here the ΔG_f^0 values of Semenov et al. (1988) and the two are in close accord at 25 °C, the latter may be more accurate at elevated temperatures and, thus, have been used in the subsequent calculations.

The temperature dependence of two limiting reactions defining datolite-danburite stability relations have been calculated using the data of Agoshkov et al. (1977), Zhdanov et al. (1977), and Semenov et al. (1988); values for the aqueous species are from SUPCRT92 (Johnson et al., 1992). Assuming that silica and B are conserved in the solid phase, datolite and danburite are related by the reaction

$$2CaBSiO_4(OH) + 2H^+ = CaB_2Si_2O_8 + Ca^{2+} + 2H_2O. \quad (12)$$

The temperature dependence of this reaction is shown in Figure 3. Paradoxically, datolite is the high-temperature calcium borosilicate under these conditions, which are probably unrealistic in natural environments. As is to be expected, high $a_{Ca^{2+}}/a^2_{H^+}$ ratios favor the crystallization of datolite. The relative stability of danburite and datolite depends on the pH of solutions. At a given $a_{Ca^{2+}}$, solutions of low pH favor the crystallization of danburite rather than datolite in accord with observations of danburite- and datolite-bearing skarns (Lisitsyn, 1973).

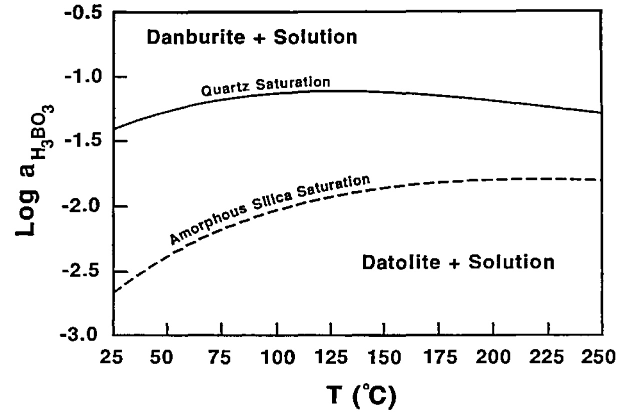

Fig. 4. Equilibrium log $a_{H_3BO_3}$ values between 25 and 250 °C at quartz and amorphous silica saturation (Walther and Helgeson, 1977) for the reaction, $CaBSiO_4(OH)$ (datolite) + SiO_2^0 + $H_3BO_3^0$ = $CaB_2Si_2O_8$ (danburite) + $2H_2O$. Datolite metastable below 100 °C.

Where Ca is conserved, datolite and danburite are related by the reaction

$$CaBSiO_4(OH) + SiO_2^0 + H_3BO_3^0 = CaB_2Si_2O_8 + 2H_2O. \quad (13)$$

This reaction is essentially independent of temperature; high H_3BO_3 activities favor the formation of danburite (Fig. 4). Because activities of $H_3BO_3^0$ must be quite high to permit the crystallization of danburite from solutions at quartz (or even amorphous silica) saturation, it is not surprising that datolite is a much more common mineral than danburite.

Inasmuch as datolite and danburite are stable with respect to calcium borates in the system CaO-B_2O_3-SiO_2-H_2O at 250 °C and 1 kbar (Kurshakova, 1982), preliminary activity diagrams of the quaternary system at 250 °C may be of interest. Two rare and probably metastable (Yang, 1990) low-temperature calcium borosilicates, bakerite, $Ca_4B_5Si_3O_{15}(OH)_3 \cdot H_2O$, and howlite, $Ca_2B_5SiO_9(OH)_5$, are not considered here. The stability relations of datolite, danburite, and wollastonite in the system CaO-B_2O_3-SiO_2-H_2O are shown in Figures 5 and 6.

An activity diagram with silica conserved in the solid phases (Fig. 5) shows again that high $a_{Ca^{2+}}/a^2_{H^+}$ ratios favor the crystallization of datolite. Thus, if calcite precipitates from solution, the stability field of datolite will be greatly restricted (Semenov et al., 1988). Datolite can form from solutions containing only small amounts of CO_2 ($a_{H_2CO_3}$ < 1 mol/L: Semenov et al., 1988), whereas the effect of CO_2 on the stability of danburite is much smaller

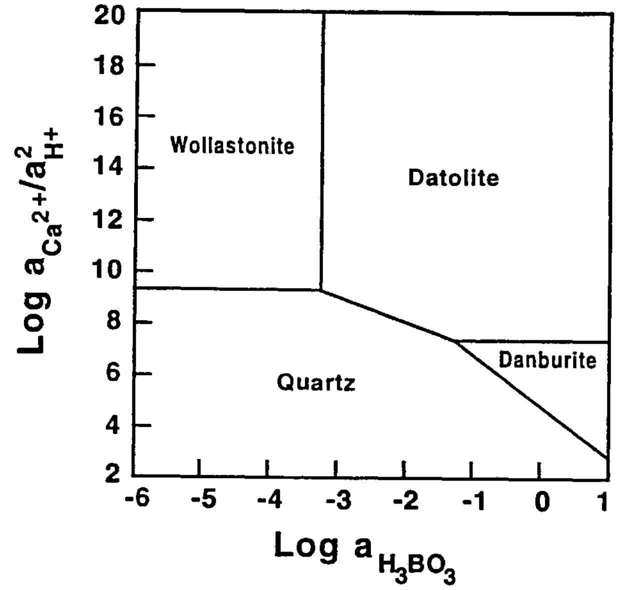

Fig. 5. Stability relations of some phases in the system CaO-B_2O_3-SiO_2-H_2O at 250 °C. SiO_2 conserved in the solid phases.

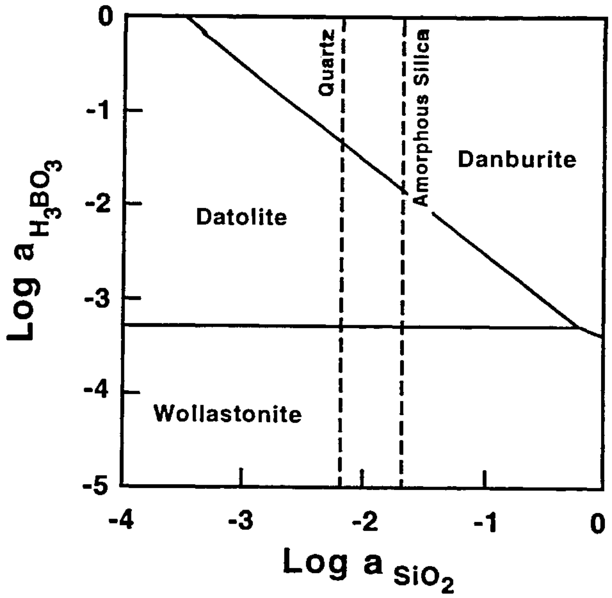

Fig. 6. Stability relations of some phases in the system CaO-B_2O_3-SiO_2-H_2O at 250 °C. Ca conserved in the solid phases.

in accord with the compositions of fluid inclusions from the Ak-Arkhan danburite deposit, Tadzhikistan (high CO_2), and Dal'negora datolite deposit, Russia (low CO_2) (Semenov et al., 1988). Thus, the crystallization of Ca-bearing minerals (e.g., calcite, gypsum) may explain the absence of datolite in evaporite deposits.

If activities of H_3BO_3 are high enough, danburite may form at relatively low $a_{Ca^{2+}}/a^2_{H^+}$ ratios (Fig. 5) or at high temperatures (Semenov et al., 1988). The high activity of H_3BO_3 necessary for the crystallization of danburite where Ca is conserved in the solid phases is illustrated in Figure 6. The minimum value of log $a_{H_3BO_3}$ for the crystallization of datolite is −3.3 (Figs. 5 and 6). These phase relations are in accord with those published by Kurshakova (1982) and Semenov et al. (1988), who showed that datolite is stable at lower H_3BO_3 activities than is danburite.

In nature, danburite is associated with granitic rocks where it forms by late-stage deuteric alteration at temperatures ≤600 °C (Kurshakova, 1982). In calc-silicate skarns it occurs as a late-stage replacement or vein mineral. Datolite is usually a later metasomatic-hydrothermal mineral in similar environments, forming often after danburite, as a result of lower or decreasing temperatures or B concentrations, particularly where activities of Ca^{2+} are high and pH is low (Kurshakova, 1982).

The appearance of danburite rather than datolite in the products of experiments with amphibolite and H_3BO_3-bearing solutions at temperatures of 550 and 600 °C (Morgan and London, 1989) is in accord with the low pH (<6) and high B-content (≥10 wt%) of the experimental solutions as well as with the presence of excess quartz and the relatively high temperatures of the experiments. However, danburite may also form as a product of diagenesis in the presence of connate brines enriched in B (Raup and Madsen, 1986), suggesting that H_3BO_3 activities exceeded the stability limit of datolite at quartz or amorphous silica saturation (Fig. 5) or that high H_3BO_3 activities coupled with low Ca^{2+} activities prevailed in the brines.

SUMMARY AND CONCLUSIONS

The present investigation, based on solubility studies, confirms earlier calorimetric studies and establishes $\Delta G^\circ_{f,298}$ of datolite at −2318 kJ/mol. The close agreement of three determinations, two experimental and one estimated, suggests a precision of less than ±1 kJ/mol. However, at elevated temperatures, the values measured by Semenov et al. (1988) and those using the method of Chermak and Rimstidt (1989), which differ by <0.1%, are probably more accurate than those determined in the present study and, therefore, have been used to define datolite-danburite stability relations.

Two reactions defining datolite-danburite stability relations where (1) silica and B and (2) Ca^{2+} are conserved provide constraints on the compositions of solutions coexisting with datolite and danburite as a function of temperature (Figs. 3 and 4). Activity diagrams at 250 °C (Figs. 5 and 6) calculated using the data of Semenov et al. (1988) delimit the stability of datolite as a function of $a_{Ca^{2+}}/a^2_{H+}$ ratios, $a_{H_3BO_3}$, and a_{SiO_2} in solution. Datolite is the stable calcium borosilicate at high $a_{Ca^{2+}}/a^2_{H^+}$ ratios, whereas high a_{SiO_2} favors danburite. While danburite is stable to higher temperatures than is datolite under most conditions (Semenov et al., 1988), the datolite-danburite boundary is temperature dependent only where H_3BO_3 and SiO_2 are conserved in the solid phases (Semenov et al., 1988; this study).

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confirm and constrain expected solution compositions based on the chemical compositions and natural occurrences of minerals in this system. However, applications of these data await detailed studies of natural datolite- and danburite-bearing assemblages.

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Appendix Table 1. Analytical results of datolite experiments

No.	*t* (d)	pH	SiO_2 (ppm)	Ca (ppm)	B (ppm)
			100 °C		
DT63*	1	8.881	30.0	10.5	4.0
DT65	3	8.400	50.0	11.0	4.2
DT35	7	8.260	58.0	11.5	5.0
DT36	21	8.049	127.0	15.0	13.9
DT06	30	7.751	140.0	25.0	20.6
DT07	60	7.862	126.0	45.0	20.8
DT55	98	8.044	515.0	22.5	9.6
DT08	123	7.840	115.0	26.0	16.5
			150 °C		
DT45	1	7.306	124.0	16.5	11.9
DT37	3	7.435	204.0	14.0	25.0
DT38	7	8.015	105.0	13.0	9.0
DT39	21	7.614	328.0	22.5	43.0
DT09	30	7.338	290.0	76.0	50.0
DT12	60	7.470	421.0	22.0	69.2
DT13	90	7.362	423.0	38.5	71.4
DT56	98	7.592	735.0	27.0	30.5
DT14	141	7.530	365.0	20.5	58.3
			200 °C		
DT46	1	7.163	321.0	13.5	29.8
DT40	3	7.374	465.0	27.5	60.0
DT42	7	7.485	506.0	30.0	63.0
DT74	15	8.282	320.0	14.5	17.0
DT41	21	7.501	533.0	26.5	71.3
DT70	30	7.589	570.0	22.5	72.5
DT30	44	7.702	295.0	16.5	38.9
DT57	82	7.528	310.0	19.0	40.0
			250 °C		
DT64	1	7.336	400.0	9.2	10.5
DT66	3	7.295	565.0	16.0	40.0
DT10	8	6.830	569.0	62.0	134.0
DT76	20	7.455	505.0	9.0	87.0
DT28	31	7.380	326.0	17.5	105.0
DT27	42	7.279	260.0	22.5	131.0
DT16	60	7.310	376.0	26.0	104.0
DT25**	72	7.128	214.0	122.0	152.0
DT72	80	7.384	535.0	14.5	95.0
DT58	98	6.830	765.0	29.0	212.0

* The solid/liquid ratio for all experiments is 0.5 g/12 mL. Unless otherwise indicated, the solid is pure datolite powder and the starting solution is distilled water.

** Solid phase = 0.5 g datolite + 0.25 g amorphous silica; liquid phase contains 0.05*M* B and 0.05*M* Ca^{2+}.