Synthesis and stability of datolite and danburite

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Synthesis and Stability of Datolite and Danburite[1])

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With 6 figures in the text and 7 tables

Abstract

Datolite, $CaBSiO_4(OH)$ and danburite, $CaB_2Si_2O_8$, were synthesized hydrothermally over a range of temperatures and pressures and their phase relations were determined in part. Optical and x-ray data of the synthetic products agree well with those of the natural minerals. At 2,000 bars water pressure the datolite + quartz $\rightleftarrows$ danburite + wollastonite + water reaction was located at $495 \pm 6°$ C. A schematic $P_{H_2O} - P_{CO_2}$ diagram elucidates the phase relations involving datolite, danburite, wollastonite, calcite, quartz and vapor. Geologic occurrences are discussed in the light of the experimental data, particularly with respect to datolite and danburite from veins, from limestone skarns and contacts and from saline environments.

Introduction

Datolite, $CaBSiO_4(OH)$[4]) and danburite, $CaB_2Si_2O_8$, are two interesting, if rare borosilicates. Both were synthesized as part of a general study of the phase relations of borosilicates (see EUGSTER and MCIVER, 1959; EUGSTER and WRIGHT, 1960). Some information was obtained on the

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[4]) CHRIST (1959) suggests that the datolite formula be written $Ca_4B_4(Si_4)_4(OH)_4$ because of its structural relationship to bakerite and garrelsite.

relative stability of these two minerals, which is helpful in the interpretation of natural assemblages.

Datolite occurs most commonly in cavities and veins in igneous rocks from granites to diabases and gabbros. It has also been found as gangue mineral in magnetite deposits (type locality at Arendale, Norway), in metamorphic limestones and in calcsilicate skarns. (See for instance DEER et al. (1961); DUNAEV, 1959; SEIM, 1961). Danburite occurrences are similar to those of datolite. It is found in dolomite (type locality at Danbury, Connecticut), in veins and clefts of granitic rocks, as gangue mineral in ore deposits. It has also frequently been found in salt deposits, associated with halite or anhydrite. (See for example GOODMAN, 1952; KÜHN and BAAR, 1955; BUDZINSKI et al., 1959; HERRMANN und HOFFMANN, 1961; FABIAN et al., 1961.)

In general datolite and danburite do not occur in the same mineral assemblage. On Piz Vallatscha, Switzerland (see P. NIGGLI et al., 1940) both were found in the same area, but in separate occurrences and appear to have formed under similar physical conditions. BARSUKOV and DERYUGINA (1961) report that datolite-danburite assemblages are common in Russia and are found as skarns in limestones, together with hedenbergite, garnet and sometimes wollastonite. HAUGHTON et al. (1939) report datolite-danburite-tourmaline-axinite assemblages from amygdales in melaphyre at the same locality.

Previous work

DE GRAMONT (1894) appears to have synthesized datolite from borax and calcium metasilicate at 400° C in a steel tube. But no positive identification is given. MOREY and INGERSON (1937) investigated the melting of danburite at atmospheric pressure. They found that danburite melts at about 1000° C to two immiscible liquids. Attempts to synthesize danburite failed. FLINT and WELLS (1936) obtained very similar results.

While our studies were in progress, BARSUKOV and DERYUGINA (1961) published a paper on the synthesis of danburite and datolite. BARSUKOV and DERYUGINA immersed limestone fragments in solutions containing borax and HCl at pressures of about 300 bars and temperatures of 300—400° C. They concluded that datolite forms preferentially in the more alkaline region (pH 8.0—8.5), while danburite predominates in the pH range from 6.3 to 8.0. These conclusions will be compared with our results in a later section (see p. 149).

Experimental procedures

Both datolite and danburite were synthesized in sealed gold tubes at water pressures of 1,000 and 2,000 bars with water as pressure medium, acting on the outside of the tubes. "Cold seal" pressure vessels similar to those described by TUTTLE (1949) were used to contain the pressure medium and were heated externally. All temperatures were continuously regulated to within $\pm 2°$ C. Individual runs yielded approximately 30 mg products. Products were identified by X-ray and optical means.

A variety of starting materials were employed. H_3BO_3 was used as source for boron, $CaCO_3$ or CaO as source for calcium and natural quartz as source for silicon. An excess of water was present in all experiments.

Fig. 1 shows a plot of the system CaO–B_2O_3–SiO_2 with H_2O projected onto this plane. The following three bulk compositions were investigated: datolite, danburite, and the composition represented by the intersection of the datolite + quartz join with the danburite + wollastonite join. The

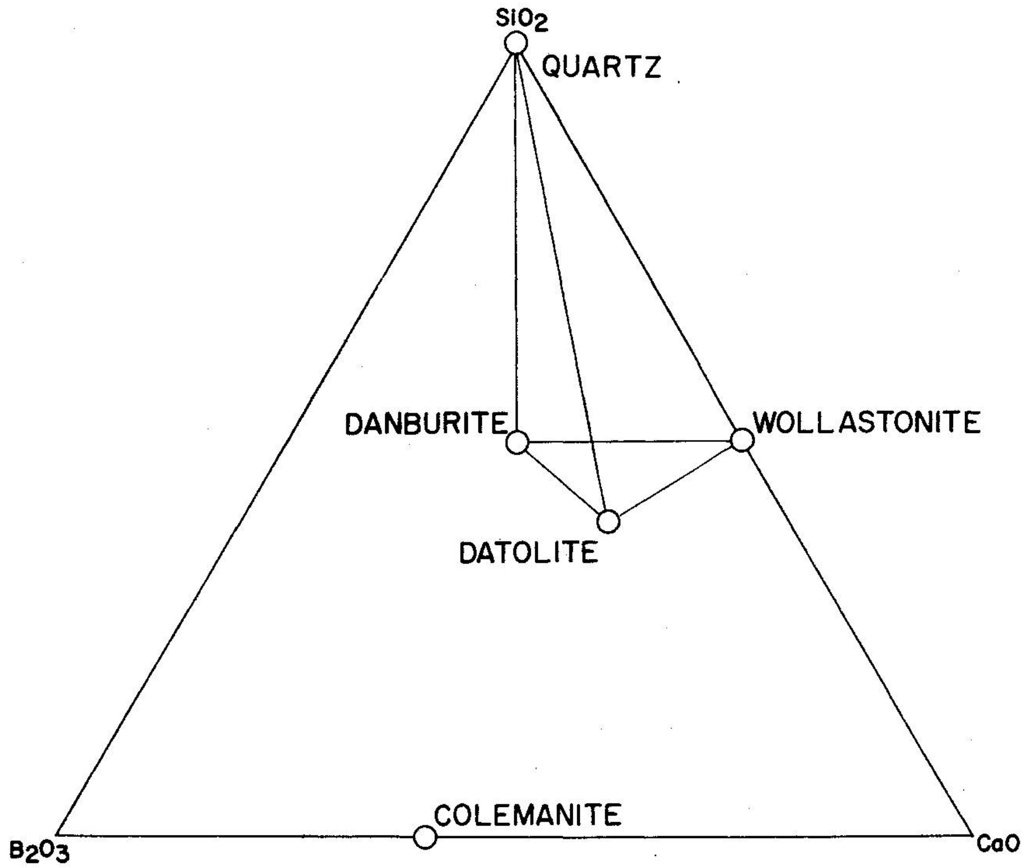

Fig. 1. System CaO-B_2O_3-SiO_2-H_2O projected from the H_2O apex, showing composition of minerals in mol %.

Table 1. *Experimental data for datolite bulk composition*

Run No.	Starting Material[1])	Temperature (°C)	Time (hours)	Solid phases obtained[2])
		$P_{total} = P_{vapor} = 2{,}000$ bars		
28	Dat Mix 2	551	145	Danb + Woll + Q
42	Syn. Dat	511	335	Dat
8	Dat Mix 1	650/506	156	Danb + unknown
48	Dat Mix 2	501	310	Dat + Danb + Woll
19	Dat Mix 1	494	160	Dat + Woll
38	Dat Mix 2	469	165	Dat + Q
7	Dat Mix 1	390	144	Dat + Q
36	Dat Mix 2	301	165	Dat + Q
20	Dat Mix 1	296	160	Dat + Woll
		$P_{total} = P_{vapor} = 1{,}000$ bars		
59	Dat Mix 2	810	70	Danb + Woll
62	Dat Mix 2	525	1870	Danb + Q
57	Dat Mix 2	505	190	Dat + tr. Danb. + tr. Woll
51	Dat Mix 2	489	215	Dat + tr. Q
34	Dat Mix 1	468	335	Dat + Danb
54	Dat Mix 2	449	260	Dat + Q

Table 2. *Experimental data for danburite bulk composition*

Run No.	Starting Material[1])	Temperature (°C)	Time (hours)	Solid phases obtained[2])
		$P_{total} = P_{vapor} = 2{,}000$ bars		
9	Nat Danb	770	107	Danb + unknown
6	Danb Mix 1	750	160	Danb + Q
18	Danb Mix 2	595	143	Danb + Q + Woll
5	Danb Mix 1	580	165	Danb
24	Danb Mix 2	522	240	Danb + Woll + Q
35	Danb Mix 2	518	165	Danb + tr. Woll
49	Danb Mix 2	501	310	Danb + Q + Woll
41	Danb Mix 2	494	165	Danb + Q + Woll
31	Danb Mix 2	490	165	Danb + Q + Woll
15	Danb Mix 2	487	235	Dat + Q
1	Danb Mix 1	480	165	Danb + Q
12	Danb Mix 2	398	235	Dat + Q
21	Danb Mix 2	296	160	Dat + Woll
27	Nat Danb	291	312	Danb
		$P_{total} = P_{vapor} = 1{,}000$ bars		
60	Danb Mix 2	810	70	Danb + Q
63	Danb Mix 2	525	1870	Danb
58	Danb Mix 2	505	190	Danb + tr. Q + tr. Woll
52	Danb Mix 2	489	215	Danb + tr. Q + tr. Woll
55	Danb Mix 2	449	260	Danb.

Table 3. *Experimental data for datolite + quartz and danburite + wollastonite bulk composition*

Run No.	Starting Material[1]	Temperature (°C)	Time (hours)	Solid phases obtained[2]
		$P_{total} = P_{vapor} = 2{,}000$ bars		
25	Nat Dat + Q	522	240	Dat + Q + Woll + tr. Danb
26	Nat Danb + Woll	522	240	Danb + Woll
43	Syn Dat + Q	511	335	Danb + Woll + Dat + Q
44	Syn Danb + Woll	511	335	Danb + Woll
46	Syn Dat + Q	502	320	Danb + Woll + tr. (Dat + Q)
47	DWDQ	501	310	Danb + Woll + tr. (Dat + Q)
39	Syn Danb + Woll	494	165	Danb + Woll + tr. (Dat + Q)
40	Syn Dat + Q	494	165	Dat + Q
29	Nat Dat + Q	490	165	Dat + Q
30	Nat Danb + Woll	490	165	Danb + Woll
16	Nat Dat + Q	487	235	Dat + Q
17	Nat Danb + Woll	487	235	Dat + Q + Danb + Woll
22	Nat Dat + Q	444	501	Dat + Q
23	Nat Danb + Woll	444	501	Danb + Woll + Q
13	Nat Dat + Q	398	235	Dat + Q
14	Nat Danb + Woll	398	235	Danb + Woll + Dat + Q
		$P_{total} = P_{vapor} = 1{,}000$ bars		
61	DWDQ	525	1870	Danb + Woll + tr. Q
56	DWDQ	505	190	Danb + Dat + Q
50	DWDQ	489	215	Dat + Q
53	DWDQ	449	260	Dat + Q

[1]) Compositions of starting materials:

Dat Mix 1: $CaO_3 + SiO_2$ fired at 1,000° C + H_3BO_3.
Dat Mix 2: $CaO + SiO_2 + H_3BO_3$.
Syn Dat: Prepared from Dat Mix at 450° C, 2,000 bars, 1 week.
Nat Dat: from Bergen Hill, N.J.
Danb Mix 1: $CaCO_3 + SiO_2 + H_3BO_3$.
Danb Mix 2: $CaO + SiO_3 + H_3BO_3$.
Syn Danb: Prepared from Danb. Mix at 600° C, 2,000 bars, 1 week.
Nat Danb: from Russel, N.Y.
DWDQ: Mix prepared from $CaO + SiO_2 + H_3BO_3$ with the composition: $2CaO \cdot B_2O_3 \cdot 3SiO_2$.

[2]) Abbreviations:

tr: trace — Dat: datolite — Q: quartz
Nat: Natural — Danb: danburite — Woll: wollastonite
Syn: Synthetic

experimental results for these bulk compositions together with the relevant run data are contained in tables 1, 2, and 3, respectively.

Datolite grows readily from mixtures of its own bulk composition at temperatures up to 500° C. However, in almost all runs a small amount of either quartz or wollastonite was also present in the products. This is obviously due to the great solubility of boric acid in the supercritical steam and reflects an appreciable difference between the bulk composition of the solids and that of the system as a whole. Excess boric acid can be added to compensate for this effect. However the excess required is different for each set of run conditions. From the few experiments available it is not possible to decide why an excess of quartz is present in some runs and an excess of wollastonite in others. Above about 500° C runs with datolite bulk composition yield danburite for reasons discussed below (see p. 146).

Danburite grows well from mixtures of its bulk composition. Traces of quartz and/or wollastonite are usually present also in the products. Several runs below 500° C using chemical mixes as starting materials yielded datolite + quartz, or datolite + wollastonite. This means either that datolite is the first reaction product and converts slowly to danburite or that so much boric acid dissolves in the vapor that the bulk composition of the solids is shifted from danburite to datolite + quartz + wollastonite. There is little doubt that danburite is stable below 500° C (see for instance run #14 at 398° C and run #27 at 291° C) and in fact at room temperature, as indicated by natural occurences (see Kühn und Baar, 1955).

Description of the Synthetic Phases

The optical and X-ray properties of synthetic danburite and datolite are very similar to those of the natural minerals. Synthetic danburite grows as prismatic crystals which reach 0.05 mm in length (figure 2). The extreme dispersion, which is characteristic of natural danburites, is also present in the synthetic ones. Refractive indeces of the danburite grown in run #63, measured in Na light are:

$$\alpha = 1.630 \pm 0.001$$
$$\beta = 1.632 \pm 0.001$$
$$\gamma = 1.634 \pm 0.002$$
$$\gamma - \alpha \approx 0.005$$

The low birefringence and the fact that β is parallel c made the determinations on the prismatic material difficult. However, the com-

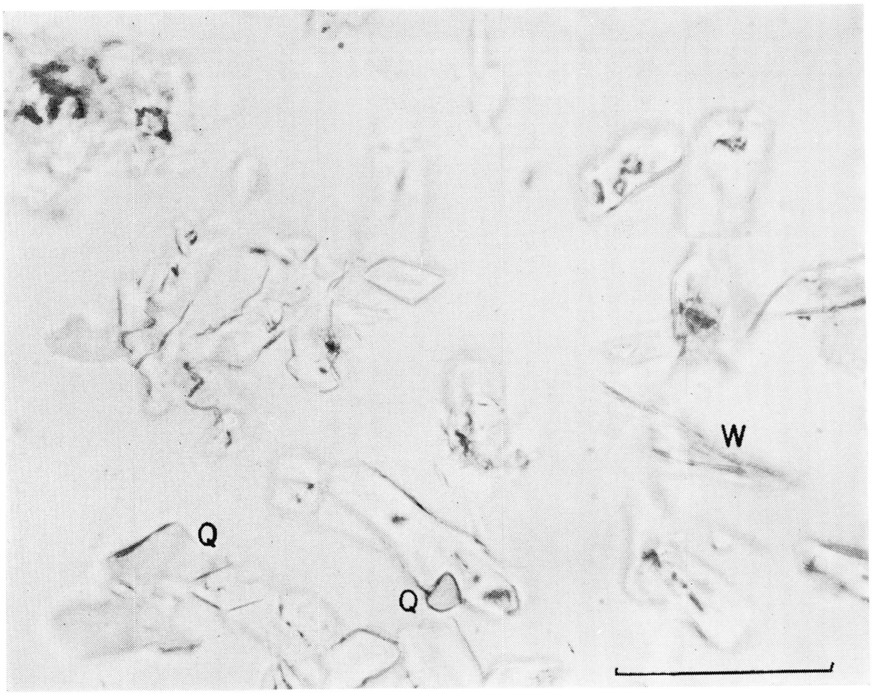

Fig. 2. Synthetic danburite from run no. 63 in an oil with a refractive index of 1.600. The c crystallographic axis ad the β-vibration direction are parallel to the long dimension of the crystals. Q = quartz, W = wollastonite, and the length of the bar is 0.05 mm. $\times 460$.

parison with values for natural material is good:

$\alpha = 1.630$
$\beta = 1.633$
$\gamma = 1.636$ (WINCHELL, 1951, p. 258)

Synthetic datolite grows in equidimensional clusters of three or four crystals up to 0.04 mm in diameter (fig. 3). The optical data for datolite from run #42 are:

$\alpha = 1.624 \pm 0.0005$
$\beta = 1.651 \pm 0.001$
$\gamma = 1.670 \pm 0.0005$
$\gamma - \alpha = 0.044$
$2\,V\,\alpha$ (calculated) $= 70°$
dispersion is weak with $r > v$

These data are similar to those of natural datolites:

$\alpha = 1.622$ to 1.626
$\beta = 1.649$ to 1.654
$\gamma = 1.666$ to 1.670
$\gamma - \alpha = 0.042$ to 0.046
$2\,V\,\alpha = 72°$ to $75°$
dispersion weak with $r > v$ (DEER et al, 1961)

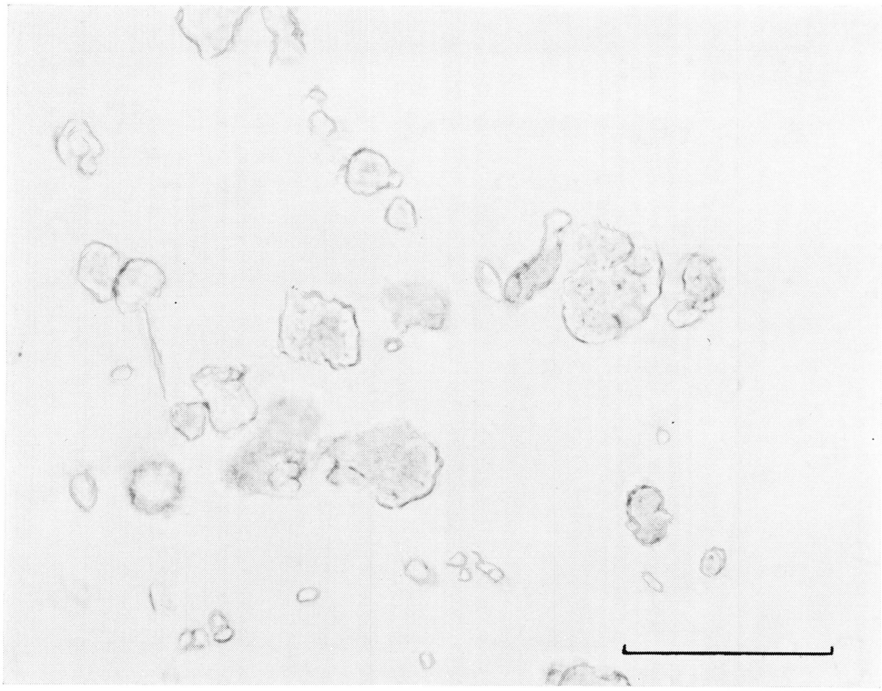

Fig. 3. Synthetic datolite from run no. 42 in an oil with a refractive index of 1.600. Several crystals of datolite form the equidimensional clusters. Length of the bar is 0.05 mm. ×460.

The X-ray powder patterns for synthetic danburites are nearly identical to those of the natural mineral. The powder data are given in table 4 and are compared to danburite from Piz Vallatscha, Switzerland

Table 4. *X-ray powder data for synthetic danburite, compared to natural danburite.* Data determined from diffractometer patterns: scanning speed $^1/_4$° and ½° per minute, CuKα radiation, LiF (a_0 = 4.0266 Å) and Si (a_0 = 5.4306 Å) internal standards.

hkl	Natural danburite (ASTM card 11—109)		Synthetic danburite run no. 63		
	d (obs)	I/I_1	d (obs)	d (calc)	I/I_1
110	5.82	5	not found	5.92	
020	4.37	5	not found	4.38	
200	4.015	15	4.025	4.018	7
120, 002	3.864	30	3.870	3.872	31
210	3.654	15	3.658	3.652	17
201	3.564	100	3.575	3.567	100
121	3.445	45	3.447	3.445	60
211	3.302	60	3.312	3.303	33
112	3.238	40	3.242	3.241	50

Table 4 (Cont.)

hkl	Natural danburite (ASTM card 11—109) d (obs)	Natural danburite I/I_1	Synthetic danburite run no. 63 d (obs)	Synthetic danburite run no. 63 d (calc)	Synthetic danburite run no. 63 I/I_1
220	2.961	70	2.967	2.961	100
022	2.900	25	2.900	2.901	21
130	2.743	70	2.747	2.744	65
031			2.738	2.732	60
212	2.654	75	2.658	2.657	52
310	2.564	25	2.566	2.562	13
013	2.473	13	2.471	2.476	10
311	2.430	25	2.435	2.432	22
113	2.370	5	2.36	2.366	5 B
230	2.363	13	2.363	2.362	14
222	2.350	30	2.352	2.352	24
	2.293	5	not found		
320	2.285	5	not found		
321 040	2.191	9	2.189	2.192 2.190	11
203	2.172	20	2.168	2.172	17
123 312	2.137	35	2.139	2.143 2.136	48
140	2.112	5	2.113	2.113	24
213	2.106	5	2.107	2.108	5
141	2.039	5	not found		
232	2.016	30	2.014	2.016	25
400	2.011	20	2.009	2.009	20
330	1.977	15	1.975	1.974	15
322	1.970	15	1.9695	1.968	15
223 401	1.945	50	1.945	1.945 1.944	21
004	1.932	20	1.936	1.936	17
411	1.900	17	1.901	1.898	9
	1.840	5	not found		
313	1.818	15	1.819	1.818	11
332	1.758	9	1.759	1.761	5
412	1.750	9	1.748	1.747	4
323 214 051	1.712	40	1.709	1.711 1.710 1.709	30
430	1.657	30	1.654	1.655	21
143			1.633	1.635	5
134			1.582	1.582	5
152			1.565	1.566	5
342			1.551	1.553	5
423			1.489	1.491	5

B: broad peak

Table 5. *Cell dimensions for synthetic danburite, compared to natural danburite*

The cell data were calculated from the powder data given in Table 4.

Natural danburite (ASTM card 11—109)	Synthetic danburite run no. 63	Natural danburite Johansson (1959)
$a_0 = 8.03$ Å	$a_0 = 8.03 \pm 0.01$ Å	$a_0 = 8.04$ Å
$b_0 = 8.77$ Å	$b_0 = 8.76 \pm 0.01$ Å	$b_0 = 7.74$ Å
$c_0 = 7.74$ Å	$c_0 = 7.74 \pm 0.01$ Å	$c_0 = 8.77$ Å
Pnam	Pnam	Pnma
density (calc) = 2.995 g/cm³	density (calc) = 2.999 g/cm³.	

(ASTM card No. 11—109). The cell dimension, calculated on the basis of Pnam (see also BAKAKIN et al., 1959) from the powder data, are

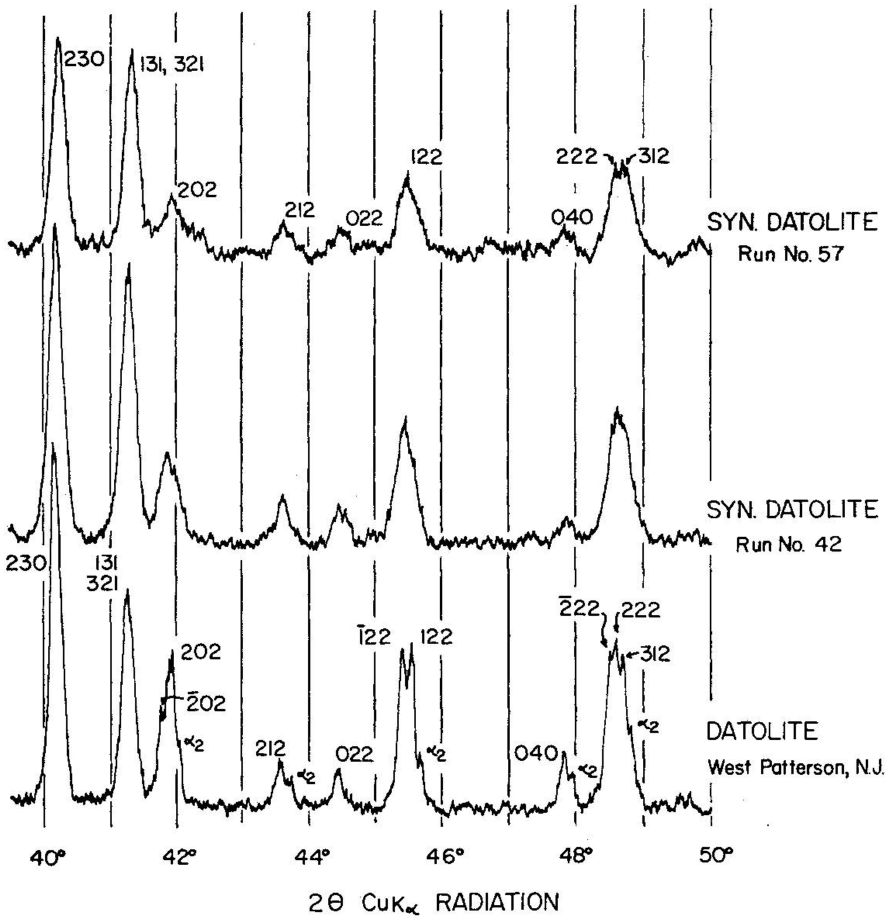

Fig. 4. Portions of x-ray diffractometer patterns of two synthetic datolites (from runs 42 and 57) and a natural datolite from West Patterson, New Jersey, to illustrate details of the peak pairs occurring between 40° and 50°, 2θ (CuKα radiation).

shown in table 5 and are essentially the same as the Piz Vallatscha danburite. Data obtained by JOHANSSON (1959) based on Pnma are also given.

There are some minor differences between the powder patterns for natural and synthetic datolites (see table 6). These differences arise from the fact that the natural datolite is better crystallized than the synthetic material and that the β angle is close to 90°. Fig. 4 is a com-

Table 6. *X-ray powder data for natural and synthetic datolites.* Determined from diffractometer patterns: scanning speed ¼° and ½° per minute, CuKα radiation, LiF (a_0 = 4.0266 Å) internal standard.

hkl	Natural datolite West Patterson, New Jersey d (obs)	d (calc)	I/I_1	Synthetic datolite run no. 41 d (obs)	d (calc)	I/I_1
110	5.97	5.97	6	5.98	5.98	9
001, 200	4.83	4.83	9	4.83	4.82	11
111	3.754	3.756	42	3.75	3.75	55
201	3.415	3.410	35	3.406	3.410	36
211	3.115	3.112	100	3.114	3.112	100
220	2.988	2.988	46	2.986	2.989	56
121	2.855	2.856	80	2.857	2.856	95
311	2.523	2.522	39	2.522	2.523	40
400	2.408	2.408	15	2.410	2.410	11
410	2.294	2.296	15	2.289	2.289	9
031	2.249	2.248	35			
230	2.246	2.246	50	2.245	2.248	51
131, 321	2.189	2.189	44	2.189	2.189	42
$\bar{2}02$	2.161	2.161	13	2.157	2.157	13
202	2.155	2.155	14			
212	2.079	2.074	12	2.076	2.075	9
022	2.040	2.039	6	2.038	2.038	5
$\bar{1}22$ (?)	1.999	1.996	24	1.995	1.992	24
122	1.993	1.994	27			
040	1.904	1.905	3	1.904	1.906	9
$\bar{2}22$	1.880	1.879	25	1.876	1.877	16
222	1.876	1.876	26			
312	1.871	1.871	24	1.871	1.870	20
041	1.772	1.772	12	1.771	1.773	13
430	1.746	1.746	4	1.746	1.749	5
132	1.721	1.721	11	1.721	1.721	13
$\bar{4}12$	1.669	1.666	12	1.665	1.664	11
412	1.664	1.661	14			
$\bar{2}32$	1.647	1.646	30			
232	1.645	1.643	36	1.645	1.644	22
$\bar{5}21$	1.622	1.621	3			

parison of portions of patterns of two synthetic datolites and a natural datolite from West Patterson, New Jersey.

Such peak pairs as $\bar{2}02$—202 and $\bar{1}22$—122 cannot be distinguished in the synthetic patterns. Therefore β is reported as 90° 00′ in table 7. The β-angle of 90° 09′ for the natural datolite was calculated on the basis of the following peaks:

$\bar{2}02$, 202, $\bar{1}22$, 122, $\bar{2}22$, 222, $\bar{4}12$, 412, $\bar{2}32$, and 232.

This value is the same as that determined by crystal morphology, but not substantiated by Ito and Mori (1953) in single crystal photographs.

Table 7. *Cell dimensions of natural and synthetic datolites*

The cell data were calculated from the powder date of Table 6.

Natural datolite West Patterson, New Jersey	Synthetic datolite run no. 41
$a_0 = 9.63 \pm 0.005$ Å	$a_0 = 9.64 \pm 0.01$ Å
$b_0 = 7.62 \pm 0.005$ Å	$b_0 = 7.62 \pm 0.01$ Å
$c_0 = 4.83 \pm 0.005$ Å	$c_0 = 4.82 \pm 0.005$ Å
$\beta = 90°\ 09'$	$\beta = 90°\ 00'$
	density (calc) = 3.000 g/cm³

Stability and phase relations

Danburite, datolite, wollastonite and quartz are related by the equation

$$\underset{\text{datolite}}{2\,CaBSiO_4(OH)} + \underset{\text{quartz}}{SiO_2} \rightleftarrows \underset{\text{danburite}}{CaB_2Si_2O_8} + \underset{\text{wollastonite}}{CaSiO_3} + H_2O \qquad (1)$$

Experiments which define the equilibrium temperature for this reaction at 2,000 bars water pressure are summarized in table 3. The equilibrium temperature lies above 494° C (run #39) and below 501° C (run #47) or at 497 ± 4° C. A slight discrepancy exists with runs 41 and 31 of table 2, at 494° and 490° C, respectively, which appear to lie on the high temperature side. Therefore a temperature of 495 ± 6° C would be consistent with all data. Data obtained at 1,000 bars water pressure are not sufficient to accurately locate another point on this univariant curve. Figure 5 summarizes the results and indicates the stable assemblages on either side of the curve.

Commonly datolite and danburite are associated with calcite rather than with wollastonite (see for instance P. Niggli et al., 1940, p. 210;

and SEIM, 1961). Therefore the stability of these minerals should be considered in the system CaO–SiO_2–B_2O_3–H_2O–CO_2. A schematic isobaric isothermal P_{H_2O}–P_{CO_2} diagram involving datolite, danburite, calcite, wollastonite and quartz is given in figure 6. Three reactions are shown:

$$\underset{\text{datolite}}{2\,CaBSiO_4(OH)} + \underset{\text{quartz}}{SiO_2} \rightleftarrows \underset{\text{danburite}}{CaB_2Si_2O_8} + \underset{\text{wollastonite}}{CaSiO_3} + H_2O \quad (1)$$

is a dehydration reaction and lies on a line parallel to the P_{CO_2} axis, with datolite + quartz on the high P_{H_2O} side.

$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{quartz}}{SiO_2} \rightleftarrows \underset{\text{wollastonite}}{CaSiO_3} + CO_2 \quad (2)$$

is a decarbonation reaction and lies on a line parallel to the P_{H_2O} axis' with calcite + quartz on the high P_{CO_2} side.

$$\underset{\text{datolite}}{2\,CaBSiO_4(OH)} + CO_2 \rightleftarrows \underset{\text{danburite}}{CaB_2Si_2O_8} + \underset{\text{calcite}}{CaCO_3} + H_2O \quad (3)$$

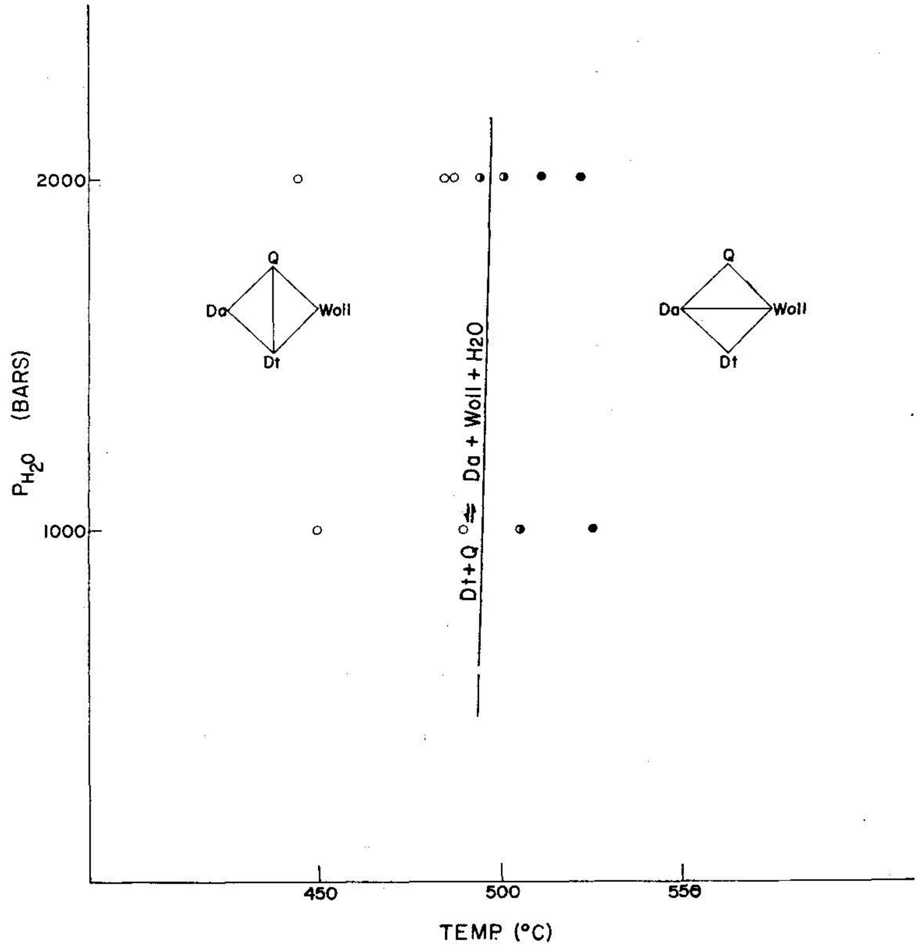

Fig. 5. P_{H_2O}-T diagram for the reaction datolite + quartz $\rightleftarrows$ danburite + wollastonite + H_2O. Da: danburite; Dt: datolite; Woll: wollastonite; Q: quartz.

involves both CO_2 and H_2O and it lies on a curve with a positive slope.

All three curves intersect at a point, at which datolite + danburite + calcite + wollastonite + quartz + vapor coexist. Since we are dealing with a five-component system, such an assemblage must lie on a univariant curve in a P-T diagram. Assuming that $P_{total} = P_{CO_2} + P_{H_2O}$, fig. 6 is an isothermal section and the intersection of the 3 curves is a point on that univariant curve.

Data for reaction (1) are given in this paper. HARKER and TUTTLE (1956) have given data for reaction (2). Combining the information available, we can derive approximate values for one point on this univariant curve: $T \approx 500°$ C, $P_{H_2O} \approx 2{,}000$ bars, $P_{CO_2} \approx 30$ bars. No data are available for reaction (3) but the slope of the curve must be near 45° in the vicinity of the isothermal invariant point.

Form the isothermal invariant point of fig. 6 six curves should radiate

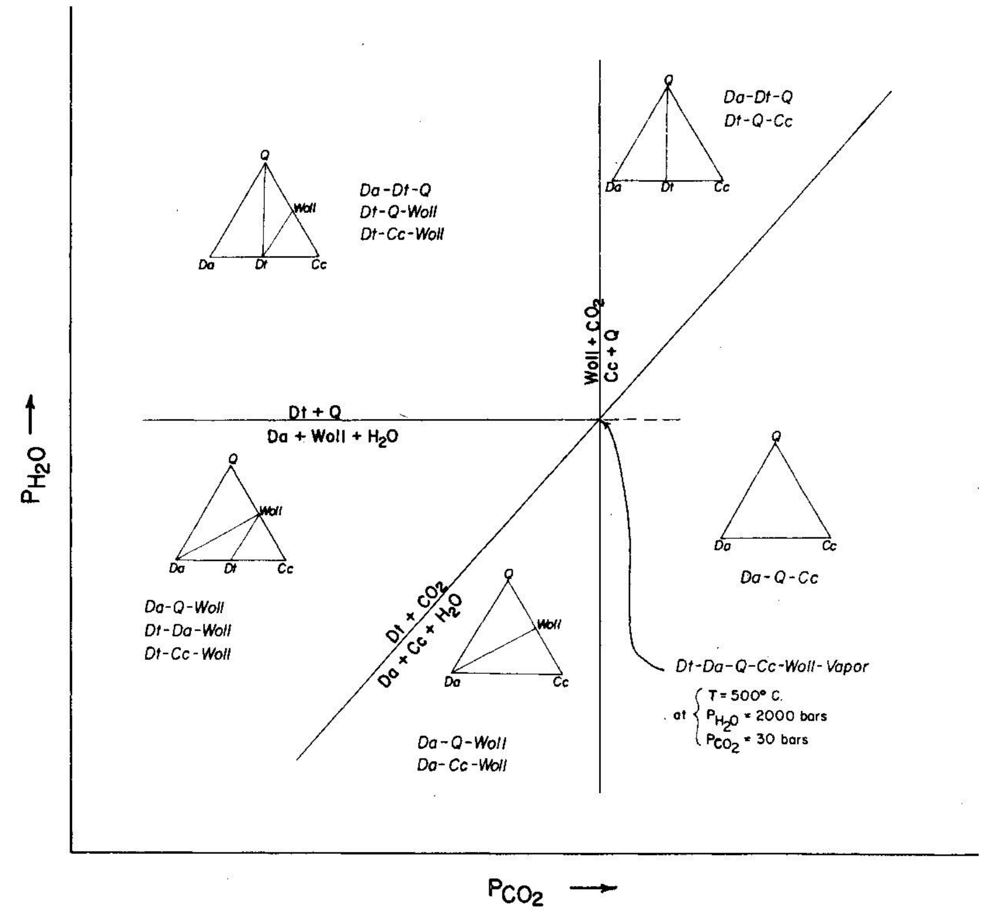

Fig. 6. Schematic isobaric-isothermal P_{H_2O}-P_{CO_2} diagram, illustrating phase relations between datolite (Dt), danburite (Da), wollastonite (Woll), calcite (Cc), and quartz (Q).

each one representing the coexistence of five phases. Because of the double degeneracy of the system, two curves merge into a single curve for reaction (2) and also for reaction (3) creating two curves which are stable on either side of the invariant point. Because of the degeneracy only four phases coexist along these two curves (datolite + danburite + calcite + vapor and calcite + wollastonite + quartz + vapor respectively). This accounts for five of the six curves. The sixth curve involves solids only and cannot be shown in fig. 6.

Fig. 6 gives the stable mineralassemblages for each of the five $P_{H_2O} - P_{CO_2}$ areas.

Datolite + calcite assemblages for instance are only possible in the high P_{H_2O} – low P_{CO_2} region, while danburite + calcite occupy the low P_{H_2O} – high P_{CO_2} region. Datolite + quartz are characteristic for high P_{H_2O} values, while danburite + quartz occur in each of the five fields.

The effect of raising the temperature is simply to displace curve (1) toward higher P_{H_2O} values and curve (2) towards higher P_{CO_2} values, without changing the essential character of fig. 6. Therefore fig. 6 is most useful in the interpretation of natural datolite and danburite assemblages. Fig. 6 also makes it possible to interpret the results obtained by Barsukov and Deryugina (1961), who obtained danburite in the more acid region (pH presumably measured at room temperature and atmospheric pressure) and datolite at higher pH values. pH is a secondary variable, since the danburite-datolite-calcite relationships are governed by P_{CO_2} and P_{H_2O}. Low pH values were created by Barsukov and Deryugina by adding more HCl to the system containing $CaCO_3$. This must have created appreciable CO_2 pressure, while high pH values correspond to low P_{CO_2} values. The results of Barsukov and Deryugina are precisely those demonstrated by fig. 6: danburite in the high P_{CO_2} (created by low pH) and datolite in the low P_{CO_2} area (created by high pH). To quantitatively interpret the datolite-danburite relationships, a detailed investigation of the reaction (3)

$$\text{datolite} + CO_2 \rightleftarrows \text{danburite} + \text{calcite} + H_2O$$

in terms of temperature, P_{CO_2}, and P_{H_2O} is necessary.

Although the experimental data are incomplete, the following conclusions can be made:

1. Both danburite and datolite can form over wide ranges of temperature. Danburite is stable to about 1,000° C at 1 atm. and to over 800° C at 1,000 bars P_{H_2O}. Datolite is stable to at least 500° C at 2,000 bars P_{H_2O}.

2. Datolite + quartz assemblages are stable up to, but not above 495° C at 2,000 bars P_{H_2O}, while danburite + quartz assemblages may cover most of the range of the danburite stability.
3. Datolite is replaced by the assemblage danburite + calcite at high P_{CO_2} and/or low P_{H_2O} values.
4. Datolite + danburite + quartz assemblages should form from the requisite bulk compositions readily over a wide range of P_{H_2O}, P_{CO_2} and T values.

Geologic applications

Detailed information on mineral assemblages containing datolite and/or danburite is scarce. However, the following generalizations can be made:

Both danburite and datolite can form over a wide range of temperatures, wherever the proper compositional requirements are met. Boron can be added by brine, hydrothermal solutions, or supercritical fluids. The environment must be high in CaO and simultaneously poor enough in Al, Mg and Fe so that tourmaline does not form instead. Compared with danburite, datolite contains slightly less B_2O_3, has a higher CaO/B_2O_3 ratio, and contains (OH) groups.

On compositional grounds alone (CaO/B_2O_3-ratio) we would therefore expect datolite to predominate in cavities and veins of basic rocks (for references see DEER et al., 1961) and danburite in granitic rocks (see for instance NIGGLI et al., 1940). Temperatures of formation for these cavity and vein fillings are usually well below the upper stability limit of datolite + quartz assemblages (see figure 5), so that datolite would form in all cases where the vein fluids had high CaO/B_2O_3 ratios and danburite where vein fluids had low CaO/B_2O_3 ratios. If this is the case, it is not clear why danburite + datolite assemblages are not commonly found in environments with intermediate CaO/B_2O_3 contents. It is, of course, possible that in some instances the datolite + quartz limit was exceeded and that danburite formed not because of lower CaO/B_2O_3 ratios in the fluid, but because of higher temperatures. If this is the case wollastonite should be associated with danburite, unless of course there is insufficient SiO_2 present.

Datolite forms in limestone skarns and contacts because of the high CaO/B_2O_3 ratios, with datolite + calcite as the common association. If, however, P_{CO_2} is raised, or the environment is very dry (low P_{H_2O}), danburite replaces datolite. This reaction can take place over a wide range of temperatures. The great majority of limestone skarns are on the datolite side of the reaction (see for instance DUNAEV, 1959; SEIM, 1961; SLAVIK and FISHER, 1903), but, as the experiments of BARSUKOV and DERYUGINA (1961) showed very convincingly, a rise in P_{CO_2} causes datolite to be replaced by danburite. Calcite is usually present in excess and stable on both sides of the reaction. Datolite + danburite + calcite assemblages are possible, but should be uncommon in nature, because for a given temperature of formation they would require very specific values of P_{CO_2} and P_{H_2O} (see figure 6).

Danburite is the borosilicate of saline environments (see KÜHN and BAAR, 1955; BUDZINSKI et al., 1959; FABIAN et al., 1961; HERRMANN und HOFFMANN, 1961) probably because of the low CaO/B_2O_3 ratios of the brines. It is unlikely that P_{H_2O} values in these low temperature environments are low enough for datolite + quartz to become unstable. Calcium is probably supplied by brines in equilibrium with sulfates, although HERRMANN and HOFFMANN (1961) demonstrated that brines associated with danburite occurrences in the Harz district have high contents of $CaCl_2$. FABIAN, GÄRTNER, and MÜLLER (1961) published photographs of danburite growing in and next to anhydrite. It remains an open question why some saline environments are characterized by calcium-borosilicates, while others, such as Searles Lake, Cal. (see GALE, 1914) or the Green River Formation (see FAHEY, 1950; and MILTON et al., 1960) show only the sodium borosilicates searlesite, $NaBSi_2O_6 \cdot H_2O$ and reedmergnerite, $NaBSi_3O_8$, present. GALE (1914) reports searlesite in intimate association with calcite. But perhaps the brines from which searlesite crystallized also showed particularly high Na_2O/CaO ratios, while those in equilibrium with danburite had much lower Na_2O contents.

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