

## CALCULATION OF ISOCHORES AND DENSITY OF BORIC ACID SOLUTIONS

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The occurrence of concentrated boric acid fluids and B-, F-, H<sub>2</sub>O-rich residual melts in many granitic pegmatites (Peretyazhko et al., 2000; Thomas et al., 2003) should affect the mineral formation processes and, in particular, the pressure as a crucial parameter that determines the stability fields of many minerals. To date, the experimental data on PVTX properties of concentrated solutions in the H<sub>2</sub>O–H<sub>3</sub>BO<sub>3</sub> system are lacking. However, some of these properties can be deduced from numerical thermodynamic modeling. The densities and P-V properties of the boric acid fluid were defined at temperature 100–700°C and pressure reaching 10 kbars (Peretyazhko, Zagorsky, 2002) by software SELECTOR. Thermodynamic properties of sassolite, H<sub>2</sub>O, H<sub>2</sub>, O<sub>2</sub>, OH<sup>-</sup>, H<sup>+</sup>, B(OH)<sub>3</sub><sup>0</sup> and B(OH)<sub>4</sub><sup>-</sup> hydrous complexes, BO<sub>2</sub><sup>-</sup>, and 23 B-bearing ideal gases were used in computations. Modeling of the equilibrium composition in the H<sub>2</sub>O–H<sub>3</sub>BO<sub>3</sub> system by means of the Gibbs isobaric–isothermal potential  $G(T,P)$  has shown that B(OH)<sub>3</sub><sup>0</sup> is the principal component of boric acid solution (pH = 3.4–4.4), and H<sub>3</sub>BO<sub>3</sub> appear to be the main gas component. Partial H<sub>3</sub>B<sub>3</sub>O<sub>6</sub> and BO<sub>2</sub><sup>-</sup> pressures are also significant, but their total contribution to the gas pressure does not exceed a few percents. In the further calculations of density and P-V properties of solutions the B-bearing gases were not taken into account, because their critical parameters are unknown. Polymerization with a formation of derivative polyboric acids (B<sub>2</sub>O(OH)<sub>5</sub><sup>-</sup>, B<sub>3</sub>O<sub>3</sub>(OH)<sub>4</sub><sup>-</sup>, B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub><sup>2-</sup>, etc.), which proceeds in concentrated boric acid solutions mainly below 50°C, was also left out of consideration. Testing models were consistent with computation results and reference data on sassolite solubility in saturated aqueous solutions with an H<sub>3</sub>BO<sub>3</sub> content of 4.64–35.19 wt% at 20–120°C. Experimental (Azizov, Akhundov, 1996) and calculated density values of 0.7m H<sub>3</sub>BO<sub>3</sub> (4.2 wt%) solution also coincide at T = 25–300 °C and P = 100–500 bar. This it suggests agreement of the data obtained with real PVTX properties of boric acid solutions at elevated temperatures and pressures.

The  $G(T,P)$  potential minimization allowed us to determine the pressure of the onset of the vapor-phase release from homogeneous saturated boric acid solutions containing from 4.64 to 35.19 wt% H<sub>3</sub>BO<sub>3</sub> and to calculate the density of these solutions (Table 1). Using the obtained volume values for boric acid solutions on curves of vapor–liquid phase equilibrium, we applied the minimization of the Helmholtz potential  $A(T,V)$  under isochoric conditions to calculate the fluid pressure and  $dP/dT$  values for temperatures up to 700 °C (Table 2). As was shown by experimental data, the increase in the H<sub>3</sub>BO<sub>3</sub> concentration shifts the critical point of the boric-acid fluid to the region of >374 °C (fluid inclusions in quartz grown from a solution with 12 wt% H<sub>3</sub>BO<sub>3</sub> were homogenized into a critical phase or gas at 401–405 °C). At high temperature and pressure, the isochores become nonlinear. At T < 300 °C, the water isochore is steeper than that of boric acid solutions. At a constant H<sub>3</sub>BO<sub>3</sub> content, the  $dP/dT$  value decreases with increasing temperature. While the temperature rise from 100 to 300°C, the isochores for water and boric acid solutions close to each other. At 305 °C, they merge, while at a reversal takes place T > 305 °C. Such isochores reversal is characteristic of many hydrous salt systems. At 305 °C, the  $dP/dT$  value remains constant and does not depend on the temperature and H<sub>3</sub>BO<sub>3</sub> content in the fluid.

Table 1. The density of boric acid solutions at liquid-vapor boundary

T, °C	H <sub>3</sub> BO <sub>3</sub> concentrations, wt% (temperature of sassolite dissolution, °C)						
	0	4,64 (20)	8,17 (40)	12,96(60)	19,05 (80)	27,54 (100)	35,19 (120)
Solution density, g/cm <sup>3</sup>							
100	0,958	0,974	0,986	1,003	1,025	1,058	1,091
125	0,939	0,955	0,967	0,984	1,006	1,039	1,071
150	0,917	0,933	0,945	0,962	0,985	1,018	1,051
175	0,892	0,908	0,921	0,938	0,961	0,996	1,029
200	0,865	0,881	0,894	0,912	0,936	0,971	1,005
225	0,834	0,849	0,863	0,882	0,906	0,943	0,979
250	0,799	0,816	0,830	0,849	0,875	0,913	0,951
275	0,759	0,777	0,789	0,810	0,837	0,878	0,917
300	0,712	0,731	0,746	0,767	0,796	0,840	0,884
325	0,655	0,675	0,691	0,715	0,747	0,798	0,850
350	0,575	0,601	0,623	0,656	0,703	0,780	0,867

As follows from thermodynamic computations, after the homogenization of solutions in fluid inclusions, the rise of H<sub>3</sub>BO<sub>3</sub> content and temperature leads to a drop in the fluid pressure in vacuoles at T<sub>hom.</sub> < 350 °C and an increase in pressure by tens and hundreds of bars at T<sub>hom.</sub> > 305 °C. Besides, while soluble component concentration in water increases, the density of solutions with H<sub>3</sub>BO<sub>3</sub> grows to a lesser extent than, for example, density of NaCl, CaCl<sub>2</sub>, KCl, LiCl, NH<sub>4</sub>Cl, NaOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>- containing solutions. Therefore, the positions of isochores for boric acid and hydrous salt solutions are substantially different, particularly, in the high P-T region.

Table 2. The  $dP/dT$  values of boric acid solutions (bar/°C) for various temperature ranges

$T_{\text{hom.}}, ^\circ\text{C}$	$\text{H}_3\text{BO}_3$ concentrations, wt% (temperature of sassolite dissolution, $^\circ\text{C}$ )						
	0	4,64 (20)	8,17 (40)	12,96 (60)	19,05 (80)	27,54 (100)	35,19 (120)
T homogenization - 300 $^\circ\text{C}$							
100	18,680	18,295	17,990	17,550	16,955	16,040	15,400
125	18,330	17,947	17,632	17,187	16,587	15,655	14,724
150	17,762	17,388	17,088	16,662	16,082	15,188	14,288
175	16,993	16,657	16,385	15,993	15,465	14,641	13,809
200	16,045	15,755	15,525	15,185	14,725	14,005	13,265
225	14,900	14,480	14,377	14,224	13,793	13,196	12,705
250	13,564	13,398	13,294	13,116	12,862	12,462	12,072
275	11,990	11,828	11,468	11,724	11,596	11,556	11,288
300	10,665	10,635	10,626	10,605	10,572	10,514	10,488
T homogenization, 300 – 500 $^\circ\text{C}$							
100	18,065	17,800	17,585	17,270	16,825	16,120	15,430
125	17,061	17,340	17,130	16,820	16,380	15,690	14,960
150	17,045	16,790	16,580	16,280	15,855	15,190	14,495
175	16,370	16,125	15,930	15,650	15,250	14,625	13,965
200	15,570	15,350	15,170	14,910	14,550	13,980	13,385
225	14,630	14,400	14,270	14,055	13,735	13,230	12,730
250	13,515	13,370	13,245	13,070	12,825	12,425	12,005
275	12,215	12,105	11,985	11,900	11,735	11,485	11,185
300	10,665	10,635	10,626	10,605	10,572	10,514	10,48
325	8,917	8,989	9,034	9,154	9,291	9,560	9,866
350	6,824	7,093	7,349	7,758	8,465	9,958	12,405
500 - 700 $^\circ\text{C}$							
100	15,530	15,375	15,245	15,055	14,785	14,340	13,895
125	15,220	15,060	14,925	14,730	14,455	14,000	13,515
150	14,830	14,665	14,535	14,340	14,065	13,615	13,120
175	14,355	14,200	14,065	13,870	13,600	13,160	12,690
200	13,785	13,630	13,500	13,320	13,065	12,645	12,200
225	13,095	12,930	12,825	12,670	12,425	12,040	11,645
250	12,275	12,155	12,055	11,915	11,710	11,380	11,025
275	11,300	11,200	11,095	11,010	10,850	10,600	10,315
300	10,140	10,085	10,050	9,985	9,895	9,750	9,580
325	8,730	8,745	8,750	8,775	8,795	8,840	8,870
350	6,920	7,095	7,245	7,480	7,830	8,455	9,230

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