

# On the Boron Concentration and Forms of Its Occurrence in Hydrothermal Ore-Forming Fluids

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**Abstract**—The boron concentration in relictant hydrothermal ore-forming fluids captured in the mineral fluid inclusions from various hydrothermal deposits (gold, gold-platinum, tin, and some others) was studied. The fluid inclusions, which were captured at various physicochemical parameters ( $T = 550\text{--}175^\circ\text{C}$ ,  $P = 3700\text{--}110$  bar), were studied with atom-emission spectroscopy (with laser unsealing of inclusions) and with aqueous extraction from the inclusions using inductively coupled plasma. The boron concentration varies strongly from 8 to 0.0001 g/kg of water, and in half of the analyses the concentration exceeds 0.5 g/kg of water. Boron occurs in solution mainly as orthoboron acid under 300–100°C, vapor-saturated pressure, and pH less than 9, according to thermodynamic modeling in a system with similar chemical composition. Possible types of soluble borate species of various elements transported by the hydrothermal ore-forming fluids are discussed.

## INTRODUCTION

The possible level of boron concentration and its soluble species in endogenic hydrothermal ore-forming fluids have been insufficiently studied. Endogenic fluids can contain superhigh boron concentrations (to 50 g/kg of water) mainly as orthoboron acid according to the occurrence of sassoline (crystalline orthoboron acid) as a captured phase in minerals from miarolitic pegmatites (Smirnov *et al.*, 1999; Smirnov *et al.*, 2000; Peretyazhko *et al.*, 2000). After these publications, sassoline was found in melt inclusions containing magmatic fluid and hosted by pegmatites related to tin-bearing granites (Thomas *et al.*, 2000). The above-mentioned findings stimulated the authors to study the boron concentration in various hydrothermal fluids, first of all in the ore-forming hydrothermal solutions at various ore deposits. Previously, only data concerning boron concentrations at the tin deposits were available (Sushchevskaya *et al.*, 1990, 2000; Reif *et al.*, 1994).

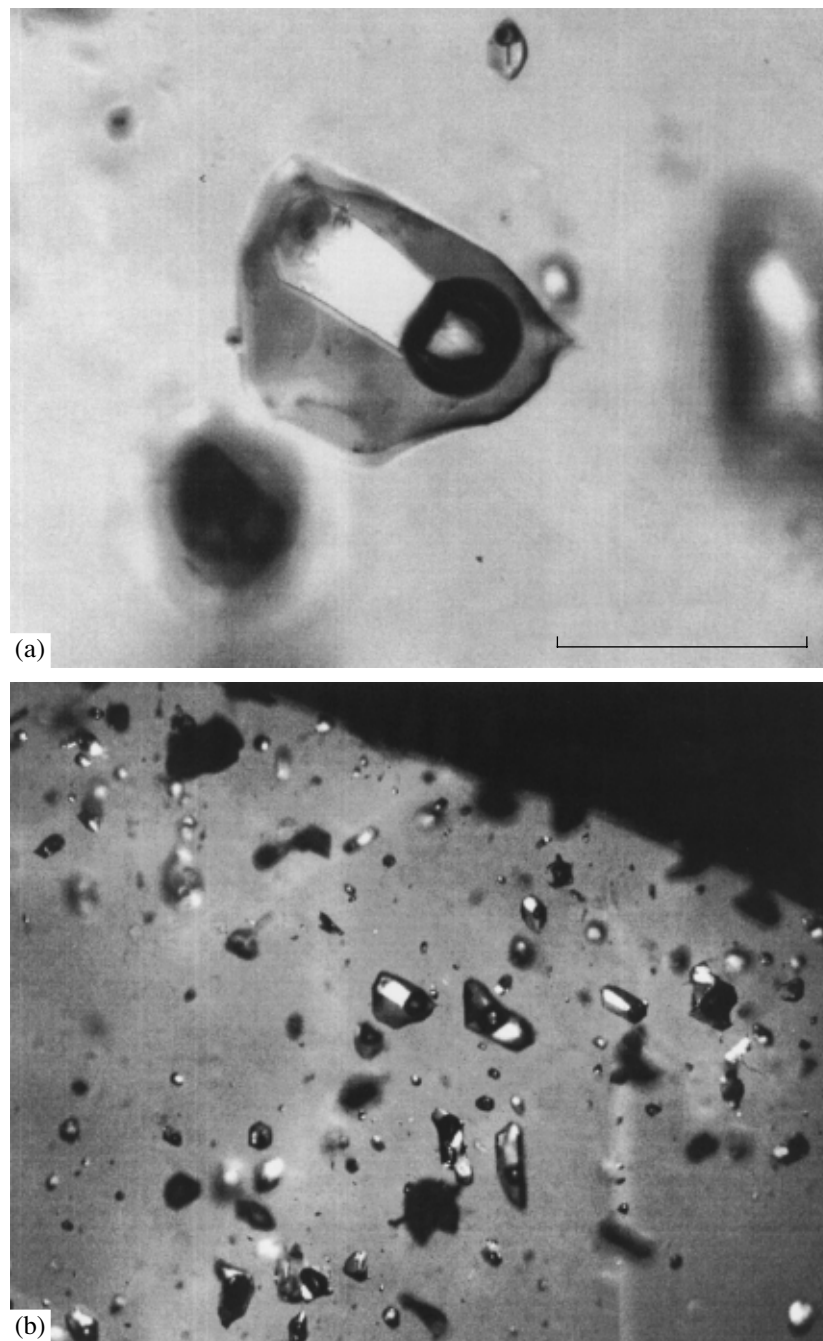
Some technical difficulties arise in the study of boron in solutions captured in the fluid inclusions, because the solution volume available for analysis is very small, the boron concentration is commonly very low, and the analytical sensitivity is low as well. The sassoline was not recognized or was confused with other substances for a long time even in boron acid brines, which contain boron their own occurrence form (Fig. 1). Only KR spectroscopy allows for its precise determination (Smirnov *et al.*, 1999; Smirnov *et al.*, 2000). Small quantities of boron acid were recognized in some samples using mass spectrometry in fluid inclusions hosted by pegmatitic minerals in California (Williams and Taylor, 1996). However, the sassoline crys-

tals were confused by the cited authors with an unusual gas hydrate, because they grow from gas bubbles, just as gas hydrates do. Later, the authors of this paper found sassoline in almost all inclusions in samples from these deposits using KR spectroscopy and estimated a much higher boron concentration than previous estimations (Peretyazhko *et al.*, 2000). Sassoline was also confused with borax (Yakubova, 1952) and fluorborates (Slivko, 1958) or was missed in the fluid inclusion descriptions.

The boron concentration in hydrothermal solutions is commonly rather low, and so it can be insufficient for boron-phase crystallization in fluid inclusions. The solubility of the orthoboron acid at room temperature is 35 g/kg of water. It corresponds to a boron concentration 6 g/kg of water. So the boron concentration (in the form of boron acid) can reach some weight percentage in common two-phase inclusions without sassoline. However, tourmaline is common in pre-ore metasomatic rocks and in early ore mineral associations at many tin, gold, and some other deposits (Kuz'min *et al.*, 1979; and others). This is the result of a rather high boron activity in ore-forming solutions. Therefore, the boron concentration was investigated in fluid inclusions from various types of deposits, and the individual fluid inclusions were studied in the same samples. The chemical thermodynamic approach was used to estimate boron-soluble species in solutions, because the most sensible analytical methods cannot determine them.

Samples from some deposits of various genesis and geochemical profile were studied: gold (Darasin in the Transbaikal Region; Berezovsk and Kochkarsk in the Urals; Olimpiada at the Eniseisk Ridge; Lebedinoe at the Central Aldan), gold-platinum (Sukhoi Log in eastern Siberia; Chudnoe in the Polar Urals; and Waterberg

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**Fig. 1.** The fluid inclusion of the boron acid brine in morion from the pegmatite vein Mika (Pamir). (a) Gas bubble, aqueous solution, and sassoline crystal are distinguishable (bar length 50  $\mu\text{m}$ ); (b) the distribution of such inclusions in the host mineral.

in South Africa), tin (Industrialnoe in the northeast part of Russia), jewelry scapolite (Kukurt in Pamir), crystal (Zhelannoe in the Polar Urals), and boron-silicate (Dal'negorsk in Primor'e).

#### METHODS

Microthermometric technics were used earlier to estimate the boron and boron-acid concentration in the solution (Peretyazhko *et al.*, 2000) for inclusions of

boron-acid brines (containing sassoline crystals at room temperature, Fig. 1). This approach included the preliminary identification of sassoline in fluid inclusions with KR spectroscopy and the subsequent measurement of the sassoline dissolution and estimation of the boron-acid concentration in fluid, taking into account the orthoboron acid solubility in various salt systems.

In the presence of subsidiary sassoline crystals in the fluid inclusions at room temperature, the solution is

saturated with boron acid, and so it is possible to estimate the boron-acid concentration by taking into account the temperature of the sassoline dissolution. The data concerning the joint solubility of boron acid with other components must be taken into account as well. The most common other components are chlorides, bicarbonates, fluorides, and sulfates of alkaline and alkaly earth metals. Today, the  $H_3BO_3$  solubility is well known for various salt systems at elevated temperatures (Peretyazhko *et al.*, 2000). The adjoining components (except KF and NaF) show moderate but effective influence on the  $H_3BO_3$  solubility if their concentration is lower than 10 wt %. Thus, the  $H_3BO_3$  concentration in saturated solutions at 25°C with added 10 wt % of salt is as follows (in wt %): 6.5 for  $K_2SO_4$ , 6.0 for  $Na_2SO_4$ , 5.5 for KCl, 4.9 for NaCl, 4.4 for  $CaCl_2$ , 3.8 for LiCl, and 2.4 for  $MgCl_2$ . This tendency remains after heating to 100°C, but the addition of the alkaly metal fluorides strongly increases the boron acid solubility due to the formation of fluor-boron complexes in solution. However, in real analytical practice, the cryometric technics allow for the recognition of 1–2 most common components but cannot determine all constituents. The system NaCl– $H_3BO_3$ – $H_2O$  is taken for calculations of the boron-acid concentration, because NaCl is one of the main components in the studied fluid inclusions. The salinity of fluid inclusions is commonly expressed in the NaCl equivalent, and so this system is especially convenient for calculations. Experimental data for this system are available in the temperature range from –21.4 to +100.1°C. Unfortunately, the subsidiary sassoline crystals were not found in minerals from the hydrothermal deposits. Such inclusions are therefore studied with other methods: atomic-emission spectroscopy after unsealing of inclusions with a laser (this is the method of the individual inclusion study) and analysis of aqueous extracts with the inductively coupled plasm technics (bulk analysis).

The individual inclusion analyses were preformed with the laser-spectral analyzer (LMA-10) in the Buryatsk Geological Institute of the Siberian Division of the Russian Academy Sciences (Ulan-Ude) by Yu.M. Ishkov. The above-mentioned method of the individual inclusion study (Ishkov and Reif, 1990) includes the following operations. The inclusion, which is localized at a depth of no more than  $\leq 20 \mu m$ , is heated to the dissolution of the gas bubble and then undergoes a laser radiation impulse. The impulse power is not sufficient to vaporize the translucent host mineral, but it increases the internal pressure in the inclusion and causes its explosion. The morphology of the resulting crater is similar to an overturned cone. The substance is ejected from the inclusion into the space between electrodes and activated with a spark discharge. The spectrograph PGS-2 takes the spectrum, which is recorded on film. Boron-acid solutions of known composition that are sealed in the resin block and fluid inclusions in the synthetic quartz are used for calibration (Reif *et al.*, 2001). The sensitivity of the

method for boron is approximately  $5 \times 10^{-11}$  g, and the total error is ~30%. Atomic-emission spectroscopy is more reliable than thermometric for complex salt solutions with unknown composition according to results of a special study (Reif *et al.*, 2001).

The analysis of aqueous extracts from fluid inclusions with inductively coupled plasma method is a multistage process. At first, individual inclusions were studied, and the predominant type of inclusions was determined in the sample. Then a monomineral fraction of 1–0.5 mm was separated. The decrepitation temperature of the majority of inclusions was estimated in the fraction. After this, the water quantity in fluid inclusions was measured with a gas chromatograph, which was necessary for calculation of the boron concentration in the solution. Then, the base solution and the extract were prepared from a 500 mg sample that had been previously washed and dried. The base solution was prepared before the vacuoles were unsealed. After this, vacuoles were thermally unsealed at 450°C, and the extract solution was prepared. The volume values of extract and base solutions are equal to each other (dilution 1 : 3). The element content was calculated as a concentration difference and recalculated to the mass of the inclusion solution. Gas analyses were performed with a Tsvet-100M chromatograph (analyst O.F. Mironova) at the Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences. The extracts were prepared and the boron content was estimated at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, with a VG Instruments quadrupole PLASMA QUAD PQ2 + TURBO mass spectrometer company (T.B. Zhukova prepared samples, and S.A. Gorbacheva was the analyst). The analytical sensitivity for boron was  $1 \times 10^{-9}$  g, and the error was 50%. Data included in Table 1 are also taken from some publications where boron concentration in the aqueous extracts is estimated by the colorimetric method with acetilquinalizarine (Nemodruk and Karalova, 1964).

The individual fluid inclusions were studied in samples before their analysis for boron. The microthermometric study was performed with a Linkam THMSG-600. The equipment allowed us to measure the phase transition temperature in the interval from –196 to +600°C and to observe these transitions under high magnifications (objective 80 $\times$  of Olympus). The salt concentration without  $CO_2$  was measured by ice or halite melting (Bodnar and Vityk, 1994). In the  $CO_2$ -containing inclusions, the salt concentration was estimated by dissolution temperature of clathrate (Collins, 1979). The chlorum concentration was calculated from the total salt concentration, taking into account the fact that NaCl predominates in solution. In some samples, Cl was determined in aqueous extracts with ion chromatography or inductively coupled plasma and then recalculated for the solution of the inclusions. The  $CO_2$  concentration was calculated by the phase-volume ratio in individual inclusions or was estimated with gas chro-

**Table 1.** The boron content in ore-forming fluids, their composition and parameters at the genetically varying hydrothermal deposits

Deposit and its type	Minerals	Sample nos.	$T_{\text{hom}}, ^\circ\text{C}$	P, bar	$C_{\text{salt}},$ g/kg of solution	$C_{\text{CO}_2},$ g/kg of solution	$C_{\text{Cl}},$ g/kg of solution	$C_{\text{B}},$ g/kg of solution $\text{H}_2\text{O}$	Method of boron estimations*	References	
Darasun, gold-porphyry, Zabaikal'e	Quartz	12VD/89	329	115	91	–	55.2**	0.83	AES LU	Authors' data	
	"	10VD/89	322	110	84	–	51.0**	1.4	AES LU	"	
Kochkarsk, gold-quartz mesothermal metamor- phosed, Urals	"	Koch1	365–338	1820–1450	79–66	281.7–110.0	47.9–40.1**	0.022	ICP MS	"	
	"	Koch1	–	–	–	–	6.1 <sup>3*</sup>	0.022	ICP MS	"	
	"	Koch1	365–338	1820–1450	79–66	281.7–110.0	47.9–40.1**	4.49	ICP MS	"	
	"	Koch1	–	–	–	43 <sup>5*</sup>	30.1 <sup>4*</sup>	4.49	ICP MS	"	
	"	Koch8	331	–	110	132.0	66.8**	0.014	ICP MS	"	
	"	Koch8	–	–	–	–	11.4 <sup>3*</sup>	0.014	ICP MS	"	
	"	Koch8	–	–	–	71 <sup>5*</sup>	70.7 <sup>4*</sup>	0.014	ICP MS	"	
	"	Koch19	347–298	1820–1040	92–73	162.8	55.8–44.3**	0.033	ICP MS	"	
	"	Koch19	347–298	1820–1040	92–73	162.8	12.1 <sup>3*</sup>	0.033	ICP MS	"	
	"	Koch29	303–288	1700–1100	28	189.2–145.2	17.0**	0.002	ICP MS	"	
	"	Koch29	–	–	–	–	3.1 <sup>3*</sup>	0.002	ICP MS	"	
Berezovsk, gold-quartz mesothermal, Urals	"	Koch29	–	–	–	144 <sup>5*</sup>	40.2 <sup>4*</sup>	0.54	ICP MS	"	
	"	TJ-2	330–290	2310–1710	104–70	193.6–171.6	63.1–42.5**	0.027	ICP MS	"	
	"	TJ-2	–	–	–	–	25.75 <sup>4*</sup>	0.027	ICP MS	"	
	"	42	335–290	2930–1500	59	215.6–136.4	35.8** 17.8 <sup>4*</sup>	0.012	ICP MS	"	
	"	3G1	275–255	1800–1470	73	184.8–140.8	44.3** 0.45 <sup>4*</sup>	0.02	ICP MS	"	
	"	262	–	–	–	–	–	0.011	ICP MS	"	
	"	4d	335–265	2860–1420	41–20	228.9–149.6	24.9–12.1**	0.015	ICP MS	"	
Olimpiada, gold-sulfide in black schists, Enisei Kryazh	"	37	300–275	2040–1520	83–66	233.3–211.2	50.4–40.1**	0.012	ICP MS	"	
	"	Ol-68	404	2090	43	83.6	26.1**	0.57	AES LU	"	
	Sukhoi Log, gold-sulfide in black schists	"	6/198.2	345–290	2260–950	76–60	237.7–206.8	46.1–36.4**	1.4	ICP MS	"
		"	6/198.2	–	–	–	–	8.2 <sup>3*</sup>	0.007	ICP MS	"
		"	6/198.2	–	–	–	67 <sup>5*</sup>	1.8 <sup>4*</sup>	0.007	ICP MS	"
"		36z/72	–	–	–	–	7.7 <sup>3*</sup>	0.004	ICP MS	"	

Table 1. (Contd.)

Deposit and its type	Minerals	Sample nos.	$T_{\text{hom}}, ^\circ\text{C}$	P, bar	$C_{\text{salt}},$ g/kg of solution	$C_{\text{CO}_2},$ g/kg of solution	$C_{\text{Cl}},$ g/kg of solution	$C_{\text{B}},$ g/kg of so- lution $\text{H}_2\text{O}$	Method of boron estimations*	References
Chudnoe, gold-palladium, Urals	Quartz	36z/72	–	–	–	490 <sup>5*</sup>	4.2 <sup>4*</sup>	0.004	ICP MS	Authors' data
	"	2/198	–	–	–	–	–	0.003	ICP MS	"
	"	6/237	380–285	2450–1340	69–67	308.0–216.1	41.9–40.7**	0.002	ICP MS	"
	"	233/00	265	–	45–42	–	27.3–25.5**	0.093	ICP MS	"
	"	233/00	–	–	–	–	24.1 <sup>4*</sup>	0.093	ICP MS	"
	"	29/98	–	–	–	–	28.2 <sup>4*</sup>	0.30	ICP MS	"
	"	3/99	–	–	–	–	178 <sup>4*</sup>	1.725	ICP MS	"
Waterberg, platinum with gold, South Africa	"	Wb-2	370–175	–	31–4	–	18.8–2.4**	0.001	ICP MS	"
Lebedinoe, gold in carbonate rocks, Aldan	"	Leb10	396	977	71	228.9	43.1**	1.94	ICP MS	"
	"	Leb10	396	–	–	12.9 <sup>5*</sup>	67.5 <sup>4*</sup>	1.94	ICP MS	"
Dalnegorsk, skarn, Primor'e	"	P-3	303–266	–	166–162	–	100.7–98.3**	8.21	ICP MS	"
	"	P-3	303–266	–	–	7.3 <sup>5*</sup>	71 <sup>4*</sup>	8.21	ICP MS	"
Zhelannoe, crystal, Urals	"	KJ-2	203	–	110	–	66.8**	0.20	ICP MS	"
	"	KJ-2	203	–	–	20.4 <sup>5*</sup>	18.9 <sup>4*</sup>	0.20	ICP MS	"
	"	KG-2	214	–	77	–	46.7**	0.11	ICP MS	"
	"	KG-2	214	–	–	268 <sup>5*</sup>	70.5 <sup>4*</sup>	0.11	ICP MS	"
Kukurt, scapolithic, Pamir	Scapolith	KUK18PL	550–505	3700–1295	668–605	35.2	405.4–367.1**	0.66–0.60	ICP MS	"
Industrial, tin quartz-tourmaline	Quartz	2541	380	–	395	56	239.7** 145 <sup>4*</sup>	5.95	ICP MS	"
Verkhnee, tin quartz-tourmaline, Primor'e	Quartz	B-40a	442	–	440	–	267.0**	0.4	AES LU	Reif <i>et al.</i> , 1994
	"	B-40a	363	–	280	–	169.9**	0.7	AES LU	"
	"	B-40	356	–	–	–	–	0.2	AES LU	"
	"	B-43	398	–	370	–	224.5**	0.5	AES LU	"

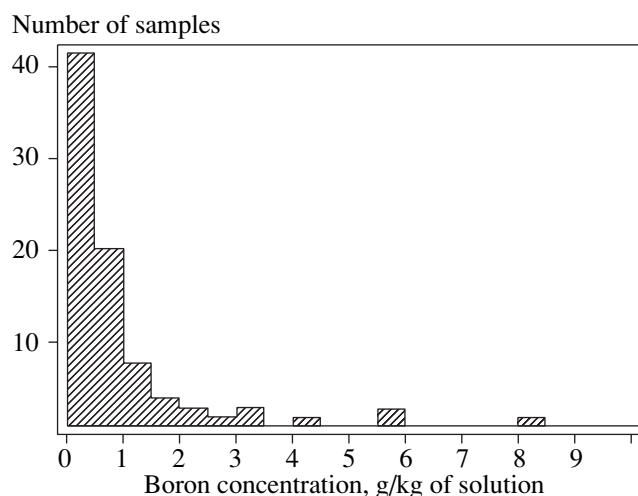
Table 1. (Contd.)

Deposit and its type	Minerals	Sample nos.	$T_{\text{hom}}, ^\circ\text{C}$	P, bar	$C_{\text{salt}},$ g/kg of so- lution	$C_{\text{CO}_2},$ g/kg of so- lution	$C_{\text{Cl}},$ g/kg of solution	$C_{\text{B}},$ g/kg of solution $\text{H}_2\text{O}$	Method of boron estimations*	References	
Solnechnoe, tin quartz-tourmaline, Primor'e	Quartz	B-39	353	–	340	–	206.3**	1.2	AES LU	Reif <i>et al.</i> , 1994	
	"	B-43	344	–	–	–	–	3.3	AES LU	"	
	"	B-43	347	–	240	–	145.6**	0.6	AES LU	"	
	"	B-43	340	–	150	–	91.0**	0.2	AES LU	"	
	Fluorite	B-40a	380	–	370	–	224.5**	2.4	AES LU	"	
	"	B-40a	380	–	420	–	254.9**	1.4	AES LU	"	
	"	B-40a	365	–	420	–	254.9**	0.3	AES LU	"	
	"	B-40a	368	–	250	–	151.7**	0.8	AES LU	"	
	"	B-40a	357	–	260	–	157.8**	1.7	AES LU	"	
	"	B-40a	358	–	260	–	157.8**	1.1	AES LU	"	
	Quartz	93-1	415	–	370	–	224.5**	1.0	AES LU	"	
	"	2533	344	–	340	–	206.3**	0.4	AES LU	"	
	"	1206	–	–	–	–	13.8 <sup>3*</sup>	0.779	ICP MS	Sushchevs- kaya <i>et al.</i> , 2000	
	"	2663	–	–	–	–	10.65 <sup>3*</sup>	0.768	ICP MS	"	
	"	2668	–	–	–	–	9.94 <sup>3*</sup>	0.627	ICP MS	"	
	Pridorozhnoe, tin quartz-tourma- line, Primor'e	"	2557a	–	–	–	–	0.422	ICP MS	"	
	Small tin-bearing ore zones, Primor'e	"	76	–	–	–	–	28.4 <sup>3*</sup>	0.801	ICP MS	"
	"	"	529	–	–	–	–	36.9 <sup>3*</sup>	5.73	ICP MS	"
	"	"	936	–	–	–	–	17.75 <sup>3*</sup>	2.38	ICP MS	"
	"	"	957	–	–	–	–	9.59 <sup>3*</sup>	0.703	ICP MS	"
Iultin, tin, quartz-tourmaline, Chukotka	"	398	–	–	–	–	–	0.660	ICP MS	"	
"	"	558	–	–	–	–	7.46 <sup>3*</sup>	0.638	ICP MS	"	
"	"	103c	–	–	–	–	8.52 <sup>3*</sup>	0.454	ICP MS	"	
"	"	112b	–	–	–	–	23.43 <sup>3*</sup>	0.303	ICP MS	"	

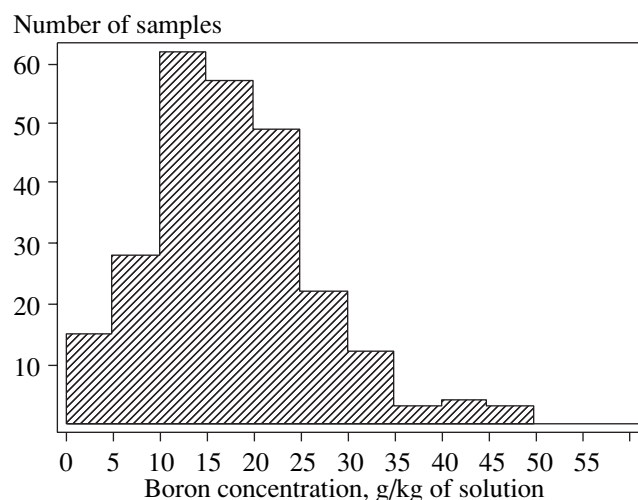
Table 1. (Contd.)

Deposit and its type	Minerals	Sample nos.	$T_{\text{hom}}, ^\circ\text{C}$	P, bar	$C_{\text{salt}},$ g/kg of so- lution	$C_{\text{CO}_2},$ g/kg of so- lution	$C_{\text{Cl}},$ g/kg of solution	$C_{\text{B}},$ g/kg of so- lution $\text{H}_2\text{O}$	Method of boron estimations*	References
Svetloe, tin, quartz-tourmaline, Chukotka	Quartz	116	—	—	—	—	—	0.725	ICP MS	Sushchev- skaya <i>et al.</i> , 2000
	"	119	—	—	—	—	6.39 <sup>3*</sup>	0.130	ICP MS	"
Akchatau, tungsten greisen, Kazakhstan	"	1300/2	—	—	—	—	—	3.46	ICP MS	"
	"	1531/3	—	—	—	—	—	0.070	ICP MS	"
	"	1518/5	—	—	—	—	—	0.941	ICP MS	"
	"	1531/3	—	—	—	—	—	0.070	ICP MS	"
Akchatau, tungsten greisen, Kazakhstan	"	22/33	—	—	—	—	—	2.60	ICP MS	"
Spokoinoe, tungsten, Zabdaikal'e	"	71	—	—	—	—	50.12	0.14	KWE	Sushchev- skaya <i>et al.</i> , 1990
	"	120	—	—	—	—	6.71	0.22	KWE	"
	"	1206	—	—	—	—	20.09	0.13	KWE	"
Solnechnoe, tin quartz-tourmaline, Primor'e	"	973	—	—	—	—	—	0.08	KWE	"
Festival, tin quartz-tourmalie, Primor'e	"	1086	—	—	—	—	64.9	1.44	KWE	"
	"	411	—	—	—	—	—	0.77	KWE	"
	"	484	—	—	—	—	26.5	1.03	KWE	"
	"	1545	—	—	—	—	6.3	0.28	KWE	"
Perevalnoe, tin, Primor'e	"	1541	—	—	—	—	62.1	0.75	KWE	"
Hingan, tin, Primor'e	"	2003	—	—	—	—	0.69	0.02	KWE	"
	"	2004	—	—	—	—	3.1	0.07	KWE	"
	Fluorite	707	—	—	—	—	5.3	0.34	KWE	"
Silinsk, tin, Primor'e	Quartz	1570	—	—	—	—	1.0	0.01	KWE	"
	"	8207	—	—	—	—	3.96	0.12	KWE	"
Khrustalnoe, tin, Primor'e	"	8041	—	—	—	—	6.0	0.08	KWE	"
	"	1856	—	—	—	—	3.36	0.16	KWE	"

\* AES LU—atomic-emission spectroscopy with laser unsealing of inclusions; ICP MS—extracts analysis by atomic-emission spectroscopy with inductively coupled plasm; CAE—colorimetric analysis of aqueous extracts; \*\* Estimations of chlorine concentration using cryometric data (recalculated for NaCl); <sup>3\*</sup> chlorine concentration estimations with ICP MS; <sup>4\*</sup> chlorine determinations with ion chromatography; <sup>5\*</sup> gas chromatography.



**Fig. 2.** Histogram of boron concentration in mineral-depositing fluids from hydrothermal ore deposits ( $n = 81$ ).



**Fig. 3.** Histogram of boron concentration in mineral-depositing fluids from miarolitic pegmatites at various regions ( $n = 255$ ).

matography. The pressure was estimated for heterogeneous fluid by intersection of isobar and isotherm (Kalyuzhnyi, 1982).

#### ESTIMATION OF THE BORON CONCENTRATION

The results of the boron concentration estimates in solutions from fluid inclusions, as well as the main parameters of these solutions, are summarized in the Table 1. The boron concentration values are also shown for the hydrothermal ore-forming fluids at some tin and tungsten deposits according to published data (Sushchevskaya *et al.*, 1990, 2000; Reif *et al.*, 1994). The sample contains 81 analyses. The analyzed fluids strongly vary in salt concentration from 668 to 4 g of

salt per 1 kg of solution (or from 405 to 0.45 g of chlorine per 1 kg of solution) and with  $\text{CO}_2$  content (490–7.3 g per 1 kg of solution). The inclusions were captured in a wide range of temperature (550–175°C) and pressure (3700–110 bar). The boron concentration widely varies from 8 to 0.0001 g per 1 kg of water, and no one extract analysis for boron by the ICP MS method shows concentration lower than the sensitivity of the method. Some analyses of the individual inclusions by emission spectroscopy do not detect the presence of boron, a result of the small solution mass available for analysis. In approximately half of the analyzed samples, the boron concentration exceeds 0.5 g/kg  $\text{H}_2\text{O}$ , and in one quarter of samples it exceeds 1 g/kg  $\text{H}_2\text{O}$  (Fig. 2). However, the boron-acid saturation level for aqueous solution (6 g/kg  $\text{H}_2\text{O}$ ) is exceeded only in one sample from the boron-silicate Dal'negorsk deposit. So, the probability of recognizing of sassoline in minerals of hydrothermal deposits is rather low.

There are no regular relations of the boron concentration to the physicochemical conditions of chlorine and  $\text{CO}_2$  concentration in analysed samples, but elevated boron concentration is typical for deposits with boron mineralization (tourmaline, axinite, and so on) in ores. Boron minerals commonly accompany the early mineral associations (quartz-tourmaline association at the Darasun and other deposits), and ore-forming fluids at these deposits are enriched with boron.

#### DISCUSSION

It is probable that the maximum concentration of boron in the endogenic fluids relates to the magmatic process, as is seen in Fig. 3 for miarolitic pegmatites. This histogram is constructed using data from Peretyazhko *et al.* (2000) and Reif *et al.* (2001). The boron concentrations in fluids are calculated by the authors and supplied with some new data for fluids in the miarolitic pegmatites from various regions of the world analyzed with various methods (a total of 255 analyses). The boron concentration in these fluids varies from 49.7 to 2.8 g/kg  $\text{H}_2\text{O}$  (most of the analyses are in the interval from 26 to 12 g/kg  $\text{H}_2\text{O}$ ). Magmatic fluids occasionally mixed with other types of solutions in the postmagmatic hydrothermal ore deposition. Such mixing strongly decreases the boron concentration in fluids. This is the reason that boron concentration reaches some tens of g/kg  $\text{H}_2\text{O}$  in pegmatitic fluids but is less than 0.5 g/kg  $\text{H}_2\text{O}$  in more than half of analyzed samples of hydrothermal ore-forming fluids. However, the boron concentration in some deposits containing tourmaline commonly exceeds 1 g/kg  $\text{H}_2\text{O}$  (the Darasun, Kochkarsk, Industrial'noe, and other deposits). Such a concentration is high enough to be taken into account in the transport forms of ore and vein components in hydrothermal fluids, because boron is an active complex-forming element.

To estimate occurrence forms of boron in solutions, the equilibrium composition of the model  $\text{H-O-B-Na-Cl}$



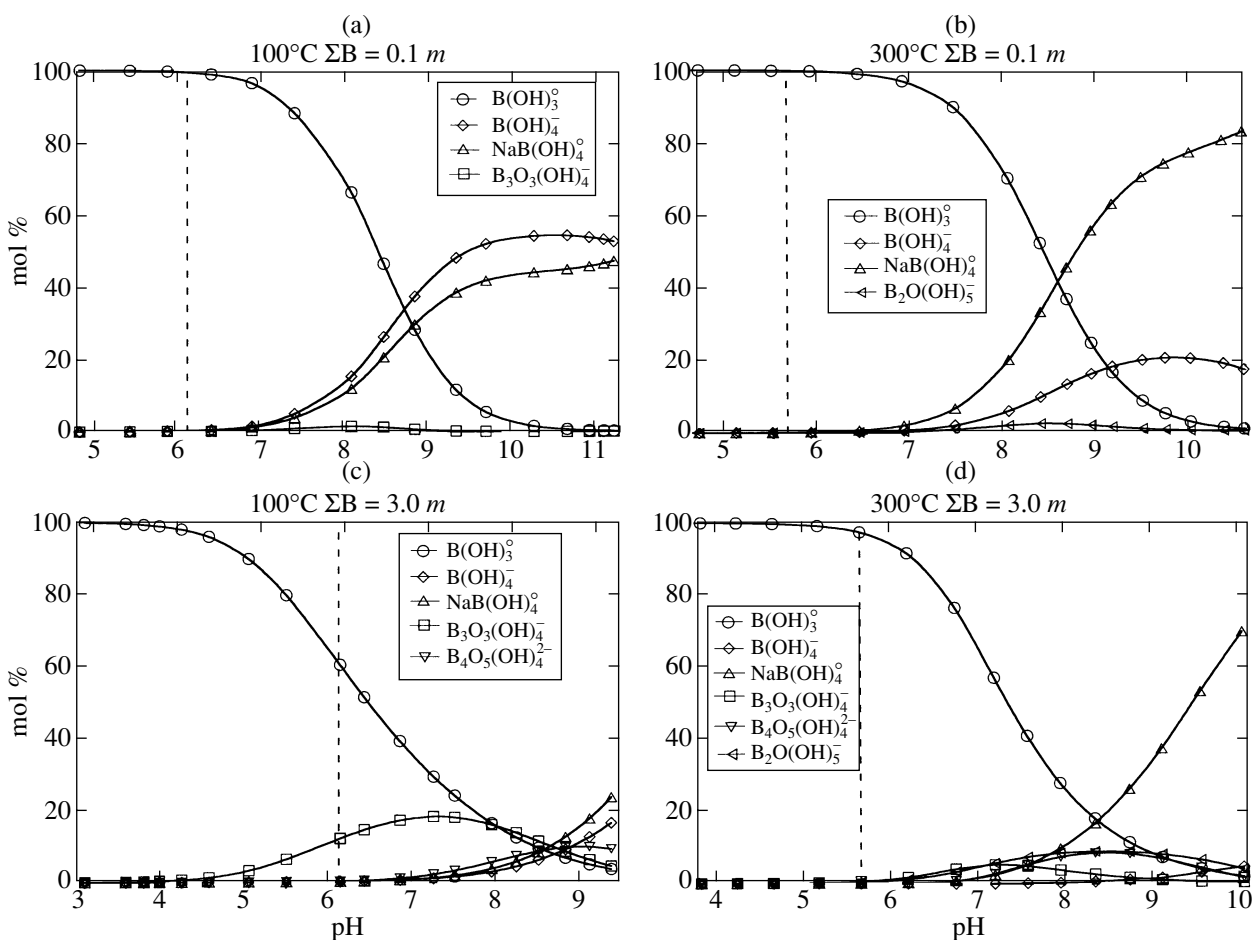
**Table 2.** The standard thermodynamic properties at 298.15 K, 1 bar, and HKF parameters of soluble species accepted in this paper

Complexes	$\Delta_f G_{298}^0$ , kal/mol	$S_{298}^0$ , kal/(mol K)	$a_1 \times 10$ , kal/(mol bar)	$a_2 \times 10^{-2}$ , kal/mol	$a_3$ , kal K/(mol bar)	$a_4 \times 10^{-4}$ , kal K/mol	$c_1$ , kal/(mol K)	$c_2 \times 10^{-4}$ , kal K/mol	$\omega \times 10^{-5}$ , kal/mol	References
$B(OH)_3^0$	-231540	38.790	8.0000	7.5000	15.0000	-6.4400	40.000	-6.8500	0	Pokrovski <i>et al.</i> , 1995
$B(OH)_4^+$	-275610	24.500	5.5200	6.3300	3.8000	-3.2500	45.000	-19.330	0.9000	"
$NaB(OH)_4^0$	-338580	39.200	6.2600	7.5100	2.8000	-3.0900	73.500	-18.930	0	"
$B_2O(OH)_5^-$	-451395	26.610	5.8668	6.5433	3.1782	-3.0495	125.88	-14.260	1.2185	Authors' data
$B_2O_3(OH)_4^-$	-571420	39.046	7.4998	10.5307	1.6109	-3.2143	56.4831	11.0510	1.0299	"
$B_4O_5(OH)_4^{2-}$	-735321	-7.744	3.8097	1.5206	5.1560	-2.8428	158.2630	39.106	3.3602	"
$Na^+$	-62591	13.960	1.8390	-2.2850	3.2560	-2.7260	18.1800	-2.9810	0.3306	Shock <i>et al.</i> , 1997
$Cl^-$	-31379	13.560	4.0320	4.8010	5.5630	-2.8470	-4.4000	-5.7140	1.4560	"
$OH^-$	-37595	-2.5600	1.2527	0.0738	1.8423	-2.7821	4.15	-10.346	1.7246	"
$NaCl^0$	-92910	28.000	5.0364	4.5189	3.9669	-2.9658	10.798	-1.3031	-0.0380	Johnson <i>et al.</i> , 1992
$NaOH^0$	-99900	10.700	2.2338	-2.3287	6.6683	-2.6826	4.0146	-3.6863	-0.0300	Shock <i>et al.</i> , 1997
$HCl^0$	-30411	0.421	16.1573	-11.4311	-46.1866	-2.3036	46.4716	-5.2811	0	Tagirov <i>et al.</i> , 1997

fluid was calculated at 100 and 300°C under pressure of saturated water vapor. The software BALANS was used for calculations of equilibria in multisystems (Akiniev, 1986, 1993). Calculations relate to two total boron concentrations 0.1 and 3.0 mol/kg, which correspond to boron concentration in ore-forming and pegmatitic fluids. The salinity is controlled by adding 1 mol/kg NaCl, and the desired pH value is reached by adding HCl or NaOH. The thermodynamic data for aqueous hydroxides  $B(OH)_3^0$ ,  $B(OH)_4^-$ , and for the complex  $NaB(OH)_4^0$  are taken from Pokrovski *et al.* (1995). The thermodynamic properties of the polycore boron complexes were determined from experimental data (Mesmer *et al.*, 1972). The alignment of the HKF model parameters (Tanger and Helgeson, 1988) for these complexes was performed with the software UT-HEL (Yu.V. Shvarov, 1995, pers. comm.). The thermodynamic parameters of the model fluids are listed in Table 2, and the results of modeling are shown in Fig. 4. The boron is mainly present in a form of orthoboron acid  $B(OH)_3^0$  in a wide pH range from neutral to slightly alkaline values. The other common species in alkaline solutions (pH > 8) are  $B(OH)_4^-$  and  $NaB(OH)_4^0$ . The role of the last one increases with rising temperature Figs. 4a, 4c. The polyboron complexes may be taken into account only at low fluid temperature ( $T < 100^\circ C$ ) even at high total boron concentration (~3 mol/kg)

(Figs. 4b, 4d). Fluids rich with boron can buffer the acidity at the level of pH ~ 3–4.

The solutions at most of the studied deposits are probably slightly acidic or neutral according to the type of metasomatic mineral associations (quartz + sericite + carbonate or quartz+carbonate with pyrite) (Zaraiskii, 1989). So, boron occurs there as orthoboron acid, if the fluor concentration is low enough. A rather high pH value and concentration of the alkaline metal borates can occur only at the Dal'negorsk skarn deposit. The metasomatic rocks with tourmaline were formed in the interaction process between hot boron-acid solution and granites (Zaraiskii, 1989), and the higher the temperature, the lower boron concentration is needed for the tourmaline formation. The high boron-acid concentration in ore fluids suggests the necessity of solving the problem of ore-metal transport in the form of borate complexes. Many borate complexes of metals are known: Ca ( $CaB(OH)_4^+$ ), Mg ( $MgB(OH)_4^+$ ), Sr ( $SrB(OH)_4^+$ ), Ba ( $BaB(OH)_4^+$ ), Co ( $Co[B(OH)_4]_4^{2-}$ ), Ni ( $Ni[B(OH)_4]_3^-$ ), Cd ( $Cd[B(OH)_4]_4^{2-}$ ), Zn ( $Zn[B(OH)_4]_4^{2-}$ ), Al ( $Al[B(OH)_4]_4^{2+}$ ), Al ( $Al[B(OH)_4]_2^+$ ), Al ( $Al[B(OH)_4]_3^0$ ), Pb ( $PbB(OH)_4^+$ ), Pb ( $Pb[B(OH)_4]_3^-$ ), Fe ( $FeB(OH)_4^{2+}$ ), Fe ( $Fe[B(OH)_4]_2^+$ ), Cu ( $CuB(OH)_4^+$ ), Cu ( $Cu[B(OH)_4]_2^0$ ), Cu ( $Cu[B(OH)_4]_3^-$ ), and Ag ( $AgB(OH)_4^0$ ) (Bassett, 1980), but their thermodynamic properties are



**Fig. 4.** Results of thermodynamic modeling of forms of boron occurrence in the system H–O–B–Na–Cl (a–d). Pressure of saturated water vapor at fixed temperature, NaCl concentration is constant and equal to 1 mol/kg. Dotted line corresponds to neutral solution at given temperature.

estimated only at room temperature. It is therefore necessary to study borate complexes experimentally at elevated temperatures, taking into account the high boron concentration in ore fluids.

### CONCLUSIONS

1. The boron concentration was studied in hydrothermal ore-forming fluids at various hydrothermal deposits under varying physicochemical parameters ( $T = 550\text{--}175^\circ\text{C}$ ;  $P = 3700\text{--}110$  bar) with various methods. The boron concentration strongly varies from 8 to 0.0001 g/kg  $\text{H}_2\text{O}$ , while in half of the analyzed samples, the concentration exceeds 0.5 g/kg  $\text{H}_2\text{O}$ .

2. At temperatures 300–100°C, pressure of saturated vapor, and pH less than 9, boron occurs in solution as orthoboron acid according to results of thermodynamic modeling.

3. The borate complexes are possible forms of transport of various elements by the hydrothermal ore-forming solutions.

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