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GEOCHEMISTRY

Composition of Ore-Bearing Fluids in the Dal'negorsk Borosilicate Deposit, Russia

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The Dal'negorsk borosilicate deposit in Primorye is the typical economic-grade calcic-skarn boron deposit [1, 2]. The large-scale mineralization is restricted to the skarnized limestones of the Upper Triassic Tetyukha Formation. The skarn zone is 3.5 km long and 500 m thick. One can distinguish the skarn (wollastonite, hedenbergite, and andradite), borosilicate (danburite, axinite, datolite, and quartz), and quartz–carbonate (quartz, calcite, apophyllite, and fluorite) stages of mineralization [1].

The study of formation conditions of borosilicate ores and composition of the ore-forming fluids is of great importance for the development of ore formation theory. The available data on chemical composition of the ore-forming fluids and physicochemical parameters of ore precipitation are constrained by the information on homogenization temperatures of fluid inclusions (FI) and contents of CO_2 and CH_4 in them [1, 2]. An understanding of the genesis of the Dal'negorsk and other similar deposits requires more complete information on composition of the ore-bearing solutions, especially on the boron content in them, and on the ore-forming role of the orthoboric acid, high contents of which were recently found in fluids that formed miarolic pegmatites with tourmaline [3]. In order to obtain this information, we used the recent methods of thermometric and analytical study of FI in the collection of minerals from the ores representing borosilicate and quartz–silicate stages. New investigation techniques of FI composition made it possible to obtain the first data on the contents of boron and other elements in the ore-forming fluids for deposits of this type.

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The studied minerals (danburite, datolite, quartz, and fluorite) contain primary, pseudosecondary, and secondary two-phase FI (120–4 μm) that are easily accessible for study. No daughter minerals optically similar to sassolite were found in the inclusions. Microthermal investigations were performed on a Linkam THMSG 600 thermocryochamber, which allowed the measurement of phase transition temperatures between –196 and 600°C. The salt contents in the inclusions were determined from ice melting temperature [4]. In addition, the composition of aqueous extracts from inclusions was studied by gas [5] and ion chromatography [6] and ICP-MS [7]. The individual inclusions were analyzed by the atomic emission spectroscopy with laser opening of FI [8] in the Geological Institute, Ulan Ude.

The thermal and cryometric investigations of the individual FI showed (Fig. 1) that minerals of the borosilicate stages formed from solutions containing Ca, Na, and Mg chlorides ($T_{eut.}$ from –69 to –35°C, estimates based on [9]) at high temperatures (danburite 337–235°C, 13.3–11.8 equiv. wt % NaCl; datolite 348–230°C, 23.3–9.2 equiv. wt % NaCl; quartz 367–266°C, 26.7–8.5 equiv. wt % NaCl). Some inclusions of the borosilicate stage contain unknown crystalline phase dissolving at temperatures from ~23 to –26°C. The minerals of the quartz–calcite stage formed from less mineralized and heated solutions: fluorite 277–252°C, 15.4–10.5 equiv. wt % NaCl; quartz 236–134°C, 26.7–8.5 equiv. wt % NaCl. No heterogenization of the solutions has been observed. With decreasing temperature, the salt content in the solution generally decreased (Fig. 1).

Chromatographic investigations revealed that the solution of the borosilicate stage contains the following components (analytical results in this paper are given in g/kg solution): CO_2 13.8–7.3, N_2 4.3–2.7, Cl 4.0–1.5, and F 1.1–0.55. The composition of solutions that formed fluorite and quartz of the quartz–calcite stage is as follows: Cl^- 3.8 g/kg, CO_2 4.85, F^- 0.48, and CH_4 0.06 (N_2 is absent). The study of aqueous extracts

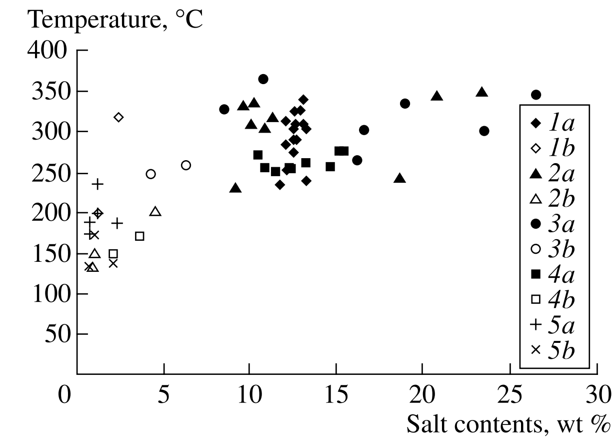

Fig. 1. Salt contents vs. temperature in the ore-forming fluid of the Dal'negorsk borosilicate deposit. (a) Primary and (b) secondary inclusions in (*1*) danburite, (*2*) datolite, and (*3*) quartz of the borosilicate stage and (*4*) fluorite and (*5*) quartz of the quartz–carbonate stage.

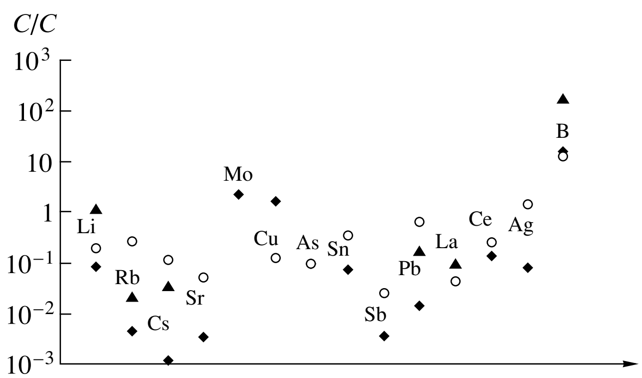

Fig. 2. Element contents in ore-forming fluids of the borosilicate stage of the Dal'negorsk borosilicate deposit vs. REE-bearing brines of the Capitan Pluton [10] (triangles), phases of highly saline solutions (diamond), and low-density gaseous fluid (circle) of the heterogeneous fluid (Sn–W–F mineralization in the Mole Granite [11]).

revealed that solutions of both stages are enriched in Li, Be, B, V, Cr, Ni, Cu, As, Rb, Sr, Y, Mo, Ag, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Eu, Ho, Er, Lu, Yb, Pb, and Au (Table 1). The solutions of the borosilicate stage are enriched in HREE (Er, Yb, Lu, Y), as well as Li, Cs, Be, Sn, and Sb, while solutions of the quartz–carbonate stage are enriched in LREE (La, Ce, Pr, Nd, Eu, Ho), as well as Rb, Sr, Mo, Cu, As, Cd, Pb, V, Cr, and Ni. The laser-spectral microanalysis of the individual fluid inclusions showed that solutions of the borosilicate stage contain the following components (g/kg solution) (Table 2): B 53.8–6.2, Cu 0.73, and Mg 3.66–0.54. Solutions of the quartz–calcite stage contain Cu (1.4–0.11), Fe (0.08), and Mg (3.45–0.09). The estimates of B and Cu contents for individual inclusions are consistent with bulk results for aqueous extracts, thus indicating that analyzed samples mainly contain primary inclusions of ore-forming fluid rather than secondary inclusions of late dilute solutions. It should be noted that the nonvariant point of datolite–danburite equilibrium was experimentally observed at a concetration of 3.75 mol orthoboric acid (or 40.5 g B) per 1 kg H_2O in the autoclave solution [1]. This observation agrees with our data.

In order to achieve a better understanding of the geochemical specifics of fluids that produced borosilicate mineralization, we compared the obtained data with similar data on the ore-bearing fluids of REE–Th–U mineralization of the Capitan Pluton, Canada [10] and Sn–W mineralization of the Mole Granite, Australia [11]. Similar information on FI is available only for these objects. Figure 2 shows the ratios of different elements in fluids of the borosilicate stage to those of aforementioned objects. It is seen that the contents of most elements in the fluids of borosilicate stage of the Dal'negorsk deposit are lower than or close to those in fluids of REE–Th–U and Sn–W mineralization. Compositionally, the ore-bearing fluid of the Dal'negorsk deposit most approximates the low-density gas phase in the heterogeneous fluid of the Sn–W mineralization in the Mole Granite. The exception is the boron content (main useful component), which is one to two orders of magnitude higher than those at other objects. In this respect, they are similar to the mineral-forming fluids of the tourmaline-bearing miarolitic pegmatites [3, 7]. However, fluid inclusions in the minerals of the pegmatites contain sassolite, whereas inclusions in minerals of the borosilicate stage do not contain daughter sassolite crystals. According to [12], sassolite from an aqueous solution of the orthoboric acid crystallized only in an acid environment. At pH >6, other borates (depending on solution composition) crystallize instead of sassolite, even if orthoboric acid may predominate in the solution. Since fluid of the Dal'negorsk deposit was in equilibrium with calcite, the absence of sassolite in fluid inclusions is natural. The aforementioned unidentified crystalline phases most likely represent the readily soluble borates, since discovered boron contents exceed its solubility at room temperature. The high boron contents in fluid agree with the boron specifics of mineralization. As was shown earlier [13], the ore-forming fluids are characterized by high contents of useful components (0.1 mol/kg solution or more). Solutions in the Dal'negorsk deposit have a concentration content of 5.0–0.5 mol/kg, which fits the ore potential criterion.

The obtained results indicate that a source with anomalously high boron content is required for the formation of the Dal'negorsk and, possibly, other similar deposits. It was shown earlier [3] that one such source may be the deeply differentiated granite magma.

Table 1. Composition of aqueous extracts from inclusions in quartz (P3) and fluorite (P13) of the Dal'negorsk deposit based on analysis by the ICP-MS method (g/kg H_2O)

Component	Borosilicate stage			Quartz–calcite stage		
	P3			P13		
	sample	background	extract	sample	background	extract
Li	0.104	0.013	0.09	0.571	0.557	0.014
Be	0.012	0	0.012	0.002	0.075	0
B	39.21	0.52	38.69	12.52	6.98	5.54
V	0.071	0	0.071	0.730	0.165	0.565
Cr	0.013	0	0.013	0.478	0.026	0.452
Mn	0.050	0.055	0	0.72	1.30	0
Co	0	0	0	0	0	0
Ni	0.464	0.332	0.132	2.35	1.77	0.58
Cu	0.373	0.0034	0.37	3.39	0.86	2.53
As	0.020	0	0.02	0.084	0	0.084
Rb	0.019	0.009	0.01	0.096	0.070	0.026
Sr	0.272	0.476	0	3.10	3.05	0.05
Y	0.005	0.00034	0.0047	0.013	0.04	0
Mo	0.022	0	0.022	0.058	0	0.058
Ag	0.004	0	0.004	0	0	0
Cd	0.0008	0	0.0008	0.12	0	0.12
Sn	0.025	0	0.025	0	0	0
Sb	0.0007	0	0.0007	0.096	0.19	0
Te	0	0	0	0	0	0
Cs	0.0044	0	0.0044	0.078	0.083	0
La	0.013	0	0.013	0.061	0.036	0.025
Ce	0.0086	0.0082	0	0.028	0	0.028
Pr	0.0039	0.0022	0.0017	0.038	0.015	0.023
Nd	0.0017	0.00114	0.00056	0.0739	0	0.074
Sm	0	0.0055	0	0	0.11	0
Eu	0.0045	0	0.0045	0.027	0.011	0.016
Gd	0	0	0	0	0.016	0
Tb	0	0.0018	0	0	0.013	0
Dy	0.0025	0.008	0	0	0.029	0
Ho	0.0009	0.0013	0	0.018	0.005	0.013
Er	0.0098	0.048	0.005	0.019	0.033	0
Tm	0.0006	0.0032	0	0.0052	0.0287	0
Lu	0.0002	0	0.0002	0.00087	0.0044	0
Yb	0.010	0	0.010	0	0.0417	0
Pb	0.101	0	0.101	1.52	0.30	1.22
U	0	0	0	0.014	0.026	0
Au	0.002	0	0.002	0.004	0	0.004

Table 2. Composition of individual inclusions in the minerals from ores of the Dal'negorsk borosilicate deposit based on analysis by atomic–emission spectroscopy with laser opening of the inclusions

Ordinal no.	Sample no.	Mineral, stage	Depth, μm	*T* hom, °C	*T* eut, °C	*T* melt of ice, °C	Equiv. NaCl, wt %	*d*, g/cm^3	FI volume, 10^{-5} cm^3	FI weight, 10^{-8} g	B	Fe	Cu	Mg
											g/kg solution			
1	P3	Quartz, 2	26	367	–52	–7.4	11.0	0.732	11.00	8.05	**6.20**	<0.05	<0.01	**0.56**
2	P3	The same	2	335	–64	–16.7	19.0	0.881	1.99	1.75	**53.80**	<0.25	<0.06	**3.66**
3	P3	"	6	259	–37	–3.9	6.3	0.846	13.80	11.67	**16.20**	<0.04	<0.01	**0.54**
4	P3	"	15	249	–31	–2.5	4.5	0.841	9.67	8.13	**23.90**	<0.05	<0.01	**0.70**
5	Qu	"	7	301	–62	–25.7	23.6	0.951	6.27	5.96	<0.20	<0.07	<0.02	**1.24**
6	Qu	"	4	328	–47.7	–5.8	8.5	0.896	4.25	3.80	<0.32	<0.11	**0.73**	**1.28**
7	Qu	"	7	164	–54	–23.4	22.7	1.076	14.86	15.99	<0.08	<0.03	**0.35**	<0.04
8	P20	Quartz, 3	16	186	–37	–0.4	0.7	0.889	25.38	22.56	<0.01	**0.08**	0.0	<0.01
9	P20	The same	12	140	–30	–1.2	2.1	0.945	4.96	4.68	<0.03	0.0	0.0	<0.04
10	P20	"	11	175	–32	–0.4	0.7	0.901	1.50	1.36	<0.09	<0.01	<0.01	<0.15
11	P6	"	2	173	–30	–0.5	0.9	0.905	2.03	1.84	<0.30	<0.08	**1.4**	**3.45**
12	P6	"	9	134	–29	–0.4	0.7	0.941	14.13	13.30	<0.04	<0.01	**0.48**	**0.59**
13	P6	"	36	188	–36	–1.3	2.2	0.897	58.27	52.27	<0.01	0.0	**0.28**	**0.35**
14	P13	Fluorite, 3	14	271	–53	–7.2	10.7	0.876	4.48	3.92	<0.41	<0.16	<0.04	**1.67**
15	P13	The same	27	255	–36	–8.5	12.3	0.909	44.38	40.34	<0.04	<0.02	**0.17**	**0.09**
16	P13	"	11	277	–37	–11.3	15.3	0.911	18.96	17.27	<0.09	<0.04	**0.11**	**0.64**
17	P13	"	4	170	–32	–2.1	3.6	0.926	52.50	48.61	<0.03	<0.01	0.0	**0.11**
18	P13	"	26	148	–36	–1.2	2.1	0.938	12.09	11.34	<0.14	<0.06	<0.01	<0.07
19	P13	"	54	257	–35	–10.7	14.7	0.926	141.93	131.43	<0.01	**0.00**	0.0	<0.01

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