

ORIGIN OF THE BORATE DEPOSITS UNDER
THE CONDITION OF HYPERGENESIS

SUN Da-peng, GAO Zhang-hong¹, MA Yuhua¹,
SHUAI kai-ye², CAI Ke-qin², GAO Jian-hua²
(1. Qinghai Institute of Salt Lakes, Academia Sinica, Xining 810008 China;
(2. China University of Geosciences (Beijing), Beijing 100083 China)

Abstract: The distribution of sedimentary boron deposits is relatively widespread in nature. They are mainly found in recent salt lakes of the North and South America and the Qinghai-Xizang (Tibet) plateau in China, some Tertiary sedimentary basins in United States of America and Turkey and in some old salt deposits in Europe. However, their origins have not been studied in detail yet. In order to investigate their formation, a lot of simulating experiments have been done using the natural brines and spring water of the saline lakes on Qinghai-Xizang plateau from 1970's. Na-borate, Na-Ca borate, Mg-borates and Mg-borate contained MgCl₂ have been obtained from 40-50 experimental samples. It is very important for illustrating the origins of the sedimentary borate deposits under the condition of hypergenesis.

- The above experimental results proved that:
- 1) The B-rich waterbodies related to geothermals and volcanicity are the substance sources of the formation of borate deposits;
 - 2) The borate deposits can be formed in various B-rich waterbodies of different aqua-salt equilibrium systems of Na, K, Mg//Cl, SO₄•H₂O and Na, K//Cl, SO₄, HCO₃, CO₃•H₂O (the salinity: 1.27-41.4%, B₂O₃: 0.05-2.97%).
 - 3) The borate deposits can be formed under the stable equilibrium environment without the metastable equilibrium (evaporating process) (nearly in deep water or buried water). At the same time, their precipitation is far later in time than that of other salt minerals for several days, several months to more than ten years.
 - 4) The low-temperature condition is beneficial to borate separation from the waterbody.
 - 5) The formation of borate deposits is closely associated with the hydrochemical type, pH value and boron content of the waterbodies.

Key Words: Borate Deposit; Hypergenesis; Origin
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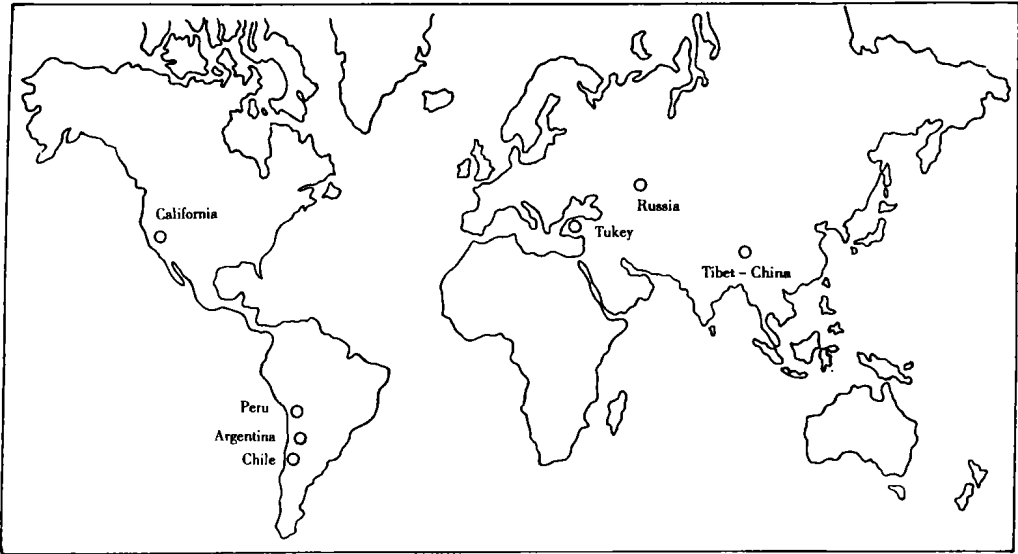


Fig.1 Current world sources of borates(After Kistler, et al., 1983)

INDROTUCTION

The Borate Deposits formed under the Condition of Hypergenesis, namely, sedimentary ones, are widespread in nature and mainly found in the recent saline lakes of the North and South America and the

Qinghai—Xizang (Tibet) Plateau of China and some Tertiary sedimentary basin in United States of America and Turkey, as well as in some old salt deposits in Europe (Fig. 1). They mainly consist of two groups of minerals: Na, Ca borates and Mg, Na—Ca borates, respectively,

Table 1 The ore minerals of borate deposits in the world

Country	Location	Age	Chemical—Type of Water—Body	Main Ore Minerals
China	Da— and Xiao—Qaidam Lake	Q	Sulphate—type	Ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$) Pinnoite ($\text{MgB}_2\text{O}_4 \cdot \text{H}_2\text{O}$)
	Zhacang—CakaLake	Q	Sulphate—type	Kurnakovite ($3\text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 15\text{H}_2\text{O}$) Pinnoite ($\text{MgB}_2\text{O}_4 \cdot \text{H}_2\text{O}$)
	Banguo—CoLake	Q	Carbonate—Type	Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
	Guojialin—CoLake	Q	Carbonate—Type	Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
	Zhabuye—CakaLake	Q	Carbonate—Type	Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
	Searls Lake	Q	Carbonate—Type	Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
United States	Boron (Kramer) Deposit	Tr	Carbonate—Type	Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
	Death Valley	Tr—Q	Carbonate—Type	Colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O} \cdot 5\text{H}_2\text{O}$)
	Emet Deposit	Tr	Carbonate—Type (?)	Colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O} \cdot 5\text{H}_2\text{O}$)
Turkey	Bigadic Deposit	Tr	Carbonate—Type (?)	Colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O} \cdot 5\text{H}_2\text{O}$)
	Kirka Deposit	Tr	Carbonate—Type	Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
	Tincalayu Borax Deposit (Argentina)	Tr	Carbonate—Type	Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
South America	Salar Pocitos (Argentina)	Q	Sulphate—Type	Ulexite ($(\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O})$)
	Salar del Hombre Muerto (Argentina)	Q	Sulphate—Type	Ulexite ($(\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O})$)
Russia	Inder Potash Deposit	P	Sulphate—Type (Marine)	Szaibelyite ($\text{MgBO}_2(\text{OH})$)
Germany	Stassfurt Potash Deposit	P	Sulphate—Type (Marine)	Boracite ($\text{Mg}_3\text{B}_7\text{O}_{13} \cdot \text{Cl}$)

The former occur in the carbonate water—body, such as Searls Lake(U·S·A), Banguo Co Lake(China), Kirka Deposit (Turkey) and Boron (Kramer) deposit (U·S·A) etc., the later in the sulphate water—body (including seawater), such as Zhacang Caka Lake (China), Da—Qaidam Lake (China), Inder Deposit (Russia) and Stassfurt Potash Daposit (Germany) and so forth (Table¹). The borate deposits were all formed to be under the condition of hypergenesis. However, in fact, their formation is related to endogenesis, especially in the boron sources, such as old volcanic rocks, volcanic activity and geothermal activity at that times. Up to now, the origins of borate deposits have not been studied in detail yet.

The origin of borates is complicated and still a base for studying the formation of boron deposits. Glushvitski and hisco—workers obtained borax, mirabilite, nahcolite and halite from the research on the aqueo—salt system $\text{Na}^+/\text{Cl}^-, \text{SO}_4^{2-}, \text{HCO}_3^-, \text{B}_4\text{O}_7$ at 0°C . Such a result has been proved by our experiments. Valyashko and Spiryagina obtained "eutectic—borate" ($\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot \text{XH}_2\text{O} \cdot y\text{MgCl}_2$) from the eutectic saturation brine ($\text{B}_2\text{O}_3: 1.2\%$) of Lake Inder after 4—years reservation. Later on, Lebeschov (1979) found boracite ($5\text{MgO} \cdot \text{MgCl}_2 \cdot 7\text{B}_2\text{O}_3$) from the isothermal evaporating experiment (30°C) of Caspian Sea water after 1—year reservation. Therefore, many scientists consider borate as the final product of seawater concentration. However, according to the results of simulating experiment, we obtained many kinds of borate minerals and proved that borate could be formed at the different stages of brine concentration (among which include the final stage of seawater concentration) (Sun et al., 1993, 1982, 1984, 1981, 1991, 1993). This paper will discuss the origins of borate deposits under the condition of hypergenesis based on the experimental results and other geological information.

EXPERIMENTAL RESEARCH

Many kinds of borates can be obtained from salt

—water solution of different compositions by artificial synthesis. However, borates have not been found in evaporating process of natural B—bearing brines, such as the isothermal evaporating experiment (25°C) of Zhacang Caka Salt Lake brine (Tibet) (Sun, et al., 1984), the natural evaporating experiment of Da—Qaidam Salt Lake brine (Qinghai) (Gao, et al., 1982), the Qinghai—Lake water experiment (Sun, et al., 1993) and so on. It explains that borates could not be precipitated directly from natural B—bearing brines (sulphate—type) under the conditions of metastable equilibrium and the normal temperature. In order to reveal the origin of borates, we have continuously carried out many experiments using the natural B—bearing brines of some salt lakes on the Qinghai—Xizang Plateau and simulating the natural conditions (especially, low—temperature) based on the borate paragenesis mineral groups in nature since 1974 (Sun, et al., 1982, 1984, 1990, 1991).

1 Materials for Experiments

The surface brine, various stage brine (salt—pool), lakeshore spring and thermal spring water of the Da—Qaidam Salt Lake, the surface brine and the bottom pressure water (mine pit water) of the Xiao—Qaidam Saline Lake, the different concentrating—stage brines of Zhacang—Caka Salt Lake and the intercrystal brine of Zabuye—Caka Salt Lake were used as the original samples of the experiments. B—soil and borax reagent were also adopted for increasing boron concentration. Distilled water ($\text{pH}=6.68$) was used in the diluting experiment. These original materials were analysed as shown in Table 2.

2 Experiments

The low temperature experiments were carried out in field and outside of laboratory in winter or using freezing plant in laboratory. Their temperature range is $12^\circ\text{C} \sim -15^\circ\text{C}$ and $-15^\circ\text{C} \sim -30^\circ\text{C}$, re-

spectively. The rest of experiments were done in laboratory and the temperature is 16℃—26℃.

The experiments are described in short as follows:

Paragenetic Mineral		Clay-Carbonate	Hydromagnesite-Northupite	Mirabilite	Mirabilite-Natron-Trona
Borax	Nature	-----	-----	-----	-----
	xperiment	-----	-----	-----	-----

a) Carbonate-type water-body

Paragenetic Mineral		Clay-Carbonate	Gypsum	Mirabilite	Halite	Bloedite-Picromerite Epsomite	Potash -- Bischofite
N A T U R E	Pinnoite	-----	-----	-----	-----	-----	-----
	Ulexite	-----	-----	-----	-----	-----	-----
	Kurnakovite	-----	-----	-----	-----	-----	-----
	Inderite	-----	-----	-----	-----	-----	-----
	Szaibelyite	-----	-----	-----	-----	-----	-----
	Boracite	-----	-----	-----	-----	-----	-----
E X P E R I M E N T	Inderite	-----	-----	-----	-----	-----	-----
	Ulexite	-----	-----	-----	-----	-----	-----
	Kurnakovite	-----	-----	-----	-----	-----	-----
	2MgO · 2B ₂ O ₃ · MgCl ₂ · 14H ₂ O	-----	-----	-----	-----	-----	-----

b) sulphate-Type water-body

Fig.2 Paragenetic Mineral Association for Borates in Nature and at the Experiments

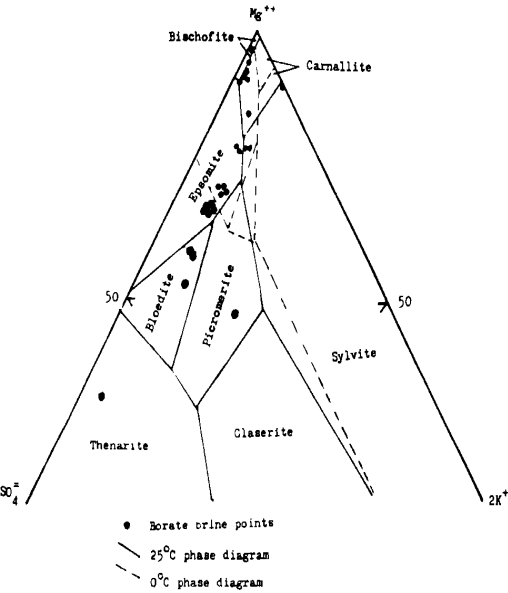


Fig. 3 Chemical composition of brines precipitated Borates from our experiments (After Sun, et al, 1984)

periment):

The experiment is to model the natural precipitating condition of borates and borate deposits at the margin zones of saline lakes, i.e. the seepage zone of spring-water (swamp belt) and the inject regions of streams and hot-springs etc. In these belts, the water-bodies are the changeable in chemical composition owing to their mixing action and also favourable to the borate formation, such as the B-ore enrichment region of the eastern shore of L. Da-Qaidam, the Kurnakovite deposit in the western shore of L. Zhacang Caka etc. Thereby, we selected some brines of various concentrating stages to mix with the spring water, hot-spring water and distilled water in order to carryout the experiment (Table. 3). From these experimental samples of different B-content (B₂O₃: 0.05—0.50%wt), pH value (7.91—9.00) and different salinity (1.27—14.76%), inderite and kurnakovite were obtained.

b. Freezing—evaporating experiment:

The main purpose of the experiment is to reveal

the condition of borate precipitation when the diluted brine is further concentrated at low temperature (Table. 4). The experiment was carried for 2—3 months in field in the winter of 1974. From the experiment, inderite and other were obtained.

c. Freezing experiment:

The experiment is simulating the natural condition of borate separation under low temperature, such as borates in paragenesis with mirabilite etc. The concentration brines of Zhacang—Caka Salt

Lake and Siling—Co Lake, as well as the intercrystal brine of Zabuye—Caka Salt Lake were used as the original samples of the experiment, which was carried out in the freezing plant of laboratory and in the outside of one in winter for several days under the temperature of -15°C — -30°C and 5°C — -15°C (Tab. 4). From the experiment, inderite and borax were obtained.

d. Unmoved—setting experiment (i.e stable environmental experiment):

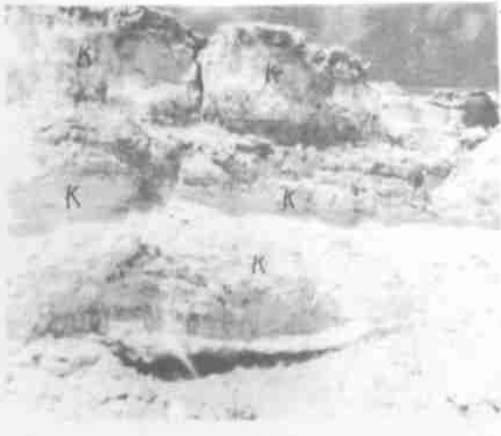
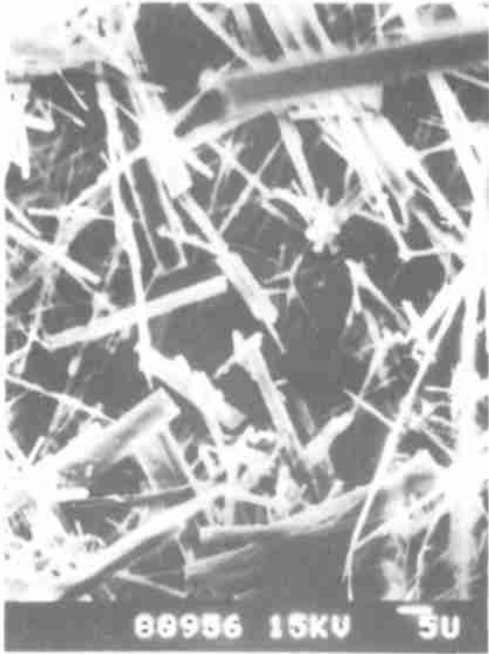


Fig. 4 Ulexite obtained from natural brines and Natural boron deposits

- A. Ulexite obtained from the Zhazang Caka Lake Brine For 12 years reservation (in lab.) (SEM $\times 800$)
- B. Ulexite obtained from the Xiao Qaidam Lake brine for 8 years reservation (in lab.) (SEM $\times 600$)
- C. Kurnakovite Deposit on the lakeshore terrace of L. Zhacang Caka (Tibet)
- D. Ulexite deposit in the east of Da—Qaidam Salt Lake (Qinghai)



E·Ulexite deposit in the mine pit of Xiao－Qaidam Salt Lake(Qinghai)·

The experiment is to study the condition of borate formation in stable water－bodies, such as in the deep water, intercrystal brine, crack and void water etc(Table 5)· In this experiment, some samples of brine were reserved in sealed bottles from several months to 12 years in laboratory (16℃－26℃)· From the experiment, ulexite, inderite and others

were obtained·

From the above experiments, two shapes of bo－rates have been obtained; One of them is good crystal and can be identified by the microscope and X－ray powder analysis, such as inderite, kurnakovite, borax and ulexite etc, which have been obtained from lower concentrated samples at or before the epsomite sepa－rated stage(pH＝neutral to basic), and the other is a crypto－crystalline aggregate (only2－3μin size)· It is always mixed with other salt minerals ·So it is dif－ficult to be distinguished from them· According to the results of chemical analysis, X－ray, infrared ab－sorption and scanning electron microscope analysis, as well as the data of the artificial systhesis, the bo－rate was calculated chemically as $2\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot \text{Mg} \cdot \text{Cl}_2 \cdot 14\text{H}_2\text{O}$ (Gao, et al. 1986), which in fact belongs to boracite species and occurs in the brines of potash－and bischofite－separating stages (pH＝4.10－5.74)(Table 5, 6)(sun, et al., 1991, 1993)

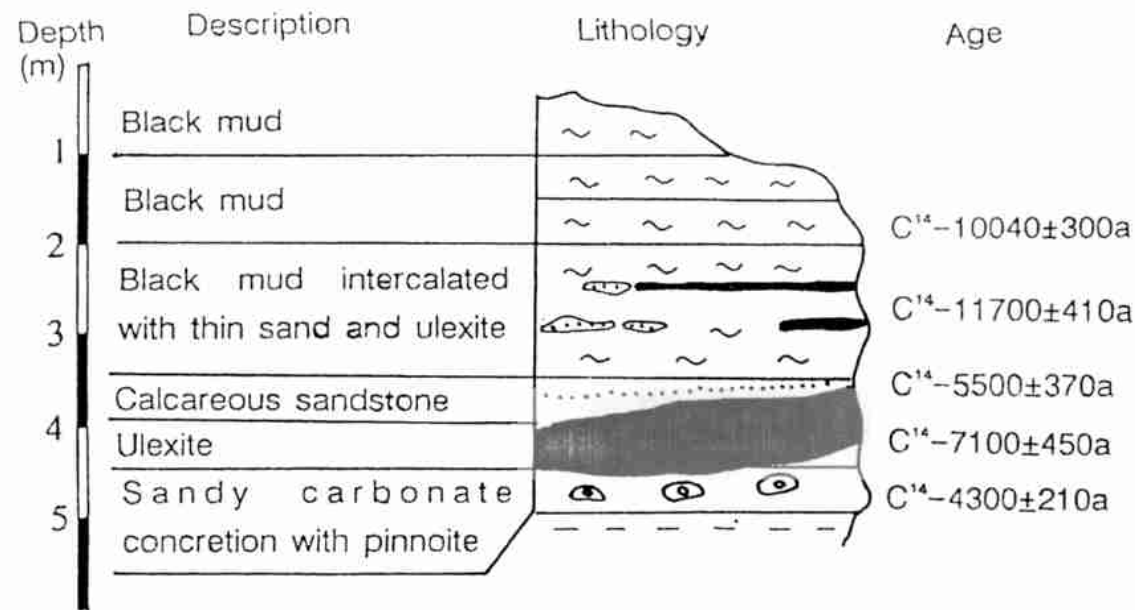


Fig.5 C^{14} dating of the sedimentary section in the B－mine pit of Xiao－Qaidam (After Sun, 1990)

ORIGIN OF BORATE DEPOSITS

1 Boron Source

Generally, there are two kinds of boron sources for the formation of borate deposits; namely geother－mal activity and volcano rocks· These sources all ex－ist in various distributive areas of boron－ore deposit in the whole world·

Table 2 The initial samples and their chemical composition of the obtained borates(After Sun, 1984)

No.	Samples*	SG/C	pH	Chemical Composition(wt%)							Total salts	Index(M/100M)			concentrating Stages
				Na	K	Mg	Ca	Cl	SO ₄	HCO ₃		CO ₃	B ₂ O ₃	2K	
D-21	Brine, Salt Pool, Da - Qai - dam Lake	1.390/27	4.99	tr.	0.09	10.02	-	24.73	3.67		2.19	0.26	91.20	6.54	Bischofite
D-20	do.	1.366/8.6	5.04	tr.	0.11	8.92	-	22.22	2.79		2.18	0.36	92.14	7.50	Carnallite
D-18	do.	1.333/18	5.44	0.06	0.31	7.82	0	20.85	3.001		1.53	1.13	90.16	8.71	do. D-19
D-17	do.	1.2759/14		4.37	1.17	3.64	0.02	14.00	6.07		0.55	29.82	65.64	27.75	Halite
D-16	do.	1.275/14		4.37	1.17	3.64	0.02	14.00	6.07		0.55	29.82	65.64	27.75	do.
D-15	do.	1.246/15	7.15	5.69	0.79	2.18	0.02	13.98	2.77		0.179	25.61	69.53	22.66	do.
D-14	do.	1.301/16	6.43	1.09	1.91	5.94	-	17.44	4.47		1.13	31.98	77.46	14.92	Epsomite
D-13	do.	1.290/15.5	6.69	2.78	1.37	4.33	0	13.08	6.88		0.27	28.71	66.67	26.97	Halite
D-12	do.	1.246/15	7.15	-	0.79	2.18	0.02	13.98	2.77		0.179	25.61	69.53	22.66	Halite
D-11	Surface Brine, L. Da - Qaidam	1.2265/15	7.49	8.15	0.41	1.24	0.094	15.02	2.29		0.195	27.41	63.50	30.0	Halite
D-10	Brine, Salt - Pool, do.	1.289/9	6.69	3.144	1.48	4.45	0.006	14.56	6.28		0.693	30.584	68.54	24.34	Halite
QE-E.	Concent. brine, L. Qinghai	1.350	6.52	1.11	2.32	6.28	-	16.02	7.36		0.698	33.10	70.8	21.06	Carnallite
QFE-5	Do.	n.d.	5.89	0.34	0.47	7.94	-	3.76	20.49		0.529	33.60	87.93	10.47	Bischofite
S-1	Spring Water East														(Unit: mg/l)
S-2	Bank, D.L.		8.34		25.78	19.29	37.9	68.4	63.4	60.7	9.7	12	297		(Unit: mg/l)
S-3	do.		8.45		630.43	76.95	50.79	643.7	340.8	315	176	179	2412		(Unit: mg/l)
	do.				1 007.7	94	198.772	1 667	1 030	272.6	79.18	282	4 130		(Unit: mg/l)
H-W	Hot - Spring, N.D.L.		8.62		312.04	29	20	480	164		52.8	1 058			(do.)
Z-12	Concent. Brine Zhacang - Cake	1.315/25		2.57	2.54	3.27	0	6.31	10.95		0.88	26.52	47.83	40.66	Bloedite - Picromerite - Halite
Z-13	do.	1.3299/25		1.71	2.35	4.19	0	6.24	11.89		1.23	27.61	52.80	38.08	Epsomite - Halite - Picromerite - Halite
Z-14	do.	1.3441/25		0.65	2.09	4.66	0	6.17	10.82		1.46	25.85	57.88	34.07	Picromerite - Epsomite - Halite
Z-15	do.	1.346/25		0.21	2.04	5.10	0	6.66	11.68		1.72	27.42	58.63	34.07	Picromerite - Epsomite - Halite - Sylvite - Halite
Z-17	do.	1.3629/25	5.5	tr.	2.02	6.41	0	8.58	8.15		2.97	28.76	70.40	22.73	Epsomite - Sylvite - Halite
Z-19	do.	1.3593/25		do.	2.25	6.01	0	8.11	3.21		2.58	28.61	66.34	25.85	do.
B-Soil	East - Lake - shore L. Da - Qaidam			29.0	1.017	0.21	0.028	31.05	14.55	7.72					

* Taken in 1974 and 1978

Table 3 The Chemical Composition of Samples Precipitated Borates in the Diluting Experiment (Sun, et al., 1984)

No.	Samples *	SG/C	pH	Chemical Composition(wt%)						Index(M/100M)				Concentrating Stages of Brine	Borate	T. P. B.
				Na	K	Mg	Ca	Cl	SO ₄	B ₂ O ₃	T. Sa.	2K	Mg	SO ₄		
D-12d	D-12 mixed with h. p. w. (1:1)	1.130/11	7.91	3.64	0.41	1.05	0.02	7.78	1.76	0.10	14.76	7.58	65.15	27.27	mirabilite(L. T)	Ca. 4 years
D-13d	D-13 with h. p. w. (1:2)	1.101/20	8.04	1.15	0.52	1.67	0.004	5.05	2.79	0.13	11.31	6.74	65.38	27.88	carbonate	Ca. 6 years
D-14d	D-14 with s. w. (1:2)	1.110/17	7.75	1.87	0.71	2.25	0.03	6.75	0.04	0.43	12.08	8.88	90.72	0.4	mirabilite(?)	Ca. 4 years
D-19d	D-19 with h. s. w. (1:2)	1.114/26	7.91	0.58	0.09	2.62	0.01	7.84	1.06	0.50	12.70	0.90	88.9	9.2	mirabilite(L. T)	3-4 months
D-12ed	D-12e with d. w. (1:10)	1.028/20	8.40	0.44	0.16	0.47	0	1.71	0.33	0.05	3.16	8.37	77.89	13.74	carbonate	kumakowite + indierite(?)
D-14ed	D-14e with d. w. (1:10)	1.032/20	8.41	0.54	0.14	0.66	0.01	1.81	0.31	0.11	3.58	5.43	84.59	9.98	carbonate	Ca. 2 years
D-18ed	D-18e with d. w. (1:10)	1.036/20	-	0.73	0.002	0.87	0.001	2.33	0.20	0.13	4.26	0.08	94.61	5.31	carbonate	3-4 years
D-19dd	D-19d with d. w. (1:10)	1.011/20	8.14	0.06	0.01	0.26	0.001	0.78	0.106	0.05	1.27	0.90	89.9	9.2	carbonate	Ca. 0.5 years
Z-12d	Z-12 with d. w. (1:10)	1.032/25	8.56	0.21	0.31	0.27	0	0.64	1.02	0.07	2.52	11.51	47.83	40.66	carbonate	indierite(?)
Z-13d	Z-13 with d. w. (1:10)	1.033/25	9.00	0.17	0.24	0.42	0	0.62	1.19	0.12	2.76	9.17	52.80	38.08	carbonate	Ca. 0.5 years
Z-14d	Z-14 with d. w. (1:10)	1.034/25	8.55	0.065	0.21	0.47	0	0.62	1.08	0.15	2.595	8.05	57.88	34.07	carbonate	Ca. 0.5 years
Z-15d	Z-15 with d. w. (1:10)	1.035/25	8.58	0.06	0.22	0.54	0	0.69	1.12	0.22	2.85	7.3	58.63	34.07	carbonate	Ca. 0.5 years
Z-17d	Z-17 with d. w. (1:10)	1.036/25	8.40	tr.	0.20	0.64	0	0.86	0.82	0.297	2.81	6.87	70.40	22.73	carbonate	3-4 months
Z-19d	Z-19 with d. w. (1:10)	1.036/25	-	0.04	0.225	0.60	0	0.81	0.92	0.25	2.86	7.81	66.34	25.85	carbonate	3-4 months

h. s. w - hot spring water; s. w. - spring water; d. w. - disillated water; S. G - specific gravity; T. P. B - Time for Precipitating Borates

Table 4 The Chemical Composition of Samples Precipitated Borates in the Freezing and Freezing Evaporation Experiment(Sun, et al., 1982, 1984, 1991)

No.	Samples *	SG/C	pH	Chemical Composition(wt%)							Index(M/100M)			Concentrating Stages of Brine	Borate	Time for Bo- rate separated	
				Na	K	Mg	Ca	Cl	SO ₄	B ₂ O ₃	T. Sa.	2K	Mg				SO ₄
Z-17f	Concentrating Brine S. L. Zhacang - Caka	1.355/25	4.96	5.48	2.04	3.7	0.01	10.5	1.4	1.49	24.61	7.88	46.4	45.7	Epsomite	Inderite + 2MgO • 2B ₂ O ₃ • MgCl ₂ • 14H ₂ O	4 days
s-9f	Concentrating Brine L. Siling - Co	1.070	9.68	2.37	0.23	0.1	0.002	1.31	2.9	0.16	0.42				Minabilite	Borax ?	2adys
Za-f	Interuystal Brine. S. L. Zabuye - Caka	1.305/20	10.86	10.7	3.83	0	0	12.3	2.19	1.45	33.3				Natron + Mirabilite	Borax	4 days
D-10e	D-10 Mixed with s. w. (1:1), f. e.	1.320/17	5.34	0.386	0.24	7.78	0	21.57	2.74	0.82	33.52	0.86	91.01	8.13	epsomite	Inderite +	- 3 months
D-11e	D-11 with s. w. (1:1), f. e.	1.261/17	7.09	4.74	1.14	3.46	0.03	14.54	5.35	0.55	29.81	6.84	66.93	26.23	halite	inderite	- 3 years
D-12e	D-12d, f. e.	1.277/20	6.32	2.79	1.63	4.70	0	17.09	3.27	0.50	29.98	8.37	77.89	13.74	halite	inderite	- 3 years
D-14e	D-14d - - B - Soil f. e.	1.318/20	5.74	tr.	1.38	6.64	0.07	18.13	3.09	1.12	30.41	5.43	84.59	9.98	epsomite	Inderite + 2MgO • 2B ₂ O ₃ • MgCl ₂ • 14H ₂ O	- 3 months
D-15e	S. W(dis. Borax) with Pool - Brine, f. e.	1.152/17	6.95	4.34	0.62	1.58	0.07	10.56	1.93	0.35	19.45	8.39	69.97	21.64	mirabilite(?)	inderite	- 3 years
D-16e	p. b(Da) + s. w. + B. s. mix. f. e.	1.287/20	6.68	2.69	1.49	4.54	0.01	14.56	5.67	0.55	29.51	7.16	70.49	22.35	halite	inderite	- 3 years
D-17e	p. b. dis. B. s., f. e.	1.293/17	6.32	1.33	1.71	5.98	-	17.78	4.43	0.60	1.83	6.93	78.34	14.73	epsomite	inderite	- 3 months
D-18e	s. w. (dis. B. s.) + p. b. f. e.	1.362/20	5.15	tr.	0.02	8.73	0.01	23.30	1.93	1.31	35.12	0.08	94.61	5.31	potash	MgO ₃ • B ₂ O ₃ • 7H ₂ O + 2MgO • 2B ₂ O ₃ • MgCl ₂ • 14H ₂ O	- 3 months

f - freezing exper iment; f. e. - freezing evaporating experiment; dis - dissolved; s. w. - spring water; F - final brine;
Experimental Condition: Z-17f, s-9f and Za-f at -25 - -30 C, -15 C and 12-17 C, respectively; D-10e to D-18e at 12 C.
- -10 C below; 2MgO · 2B₂O₃ · MgCl₂ · 14H₂O and MgO · 3B₂O₃ & H₂O were determined initially after chemical analysis etc(Sun, et al., 1991).

Table 5 The Chemical Composition of Samples Precipitated Borates in the Unmoved - Setting Experiment(Sun, et al., 1982, 1984, 1990, 1991, 1993)

No.	Samples *	SG/C	pH	Chemical Composition(wt%)							Index(M/100M)				Concentrating Stages of Brine	Borate	Time for Bo- rate separated
				Na	K	Mg	Ca	Cl	SO ₄	B ₂ O ₃	T. Sa.	2K	Mg	SO ₄			
X-1	Mine Pit Brine, S. L. Xiao - Qaidam	1.095/16	8.30	3.75	0.16	0.44	0.05	6.2	1.52	0.15	12.28	5.6	50.0	44.4	Mirabilite + Halite	Ulexite	3 years
X-2	Surface Brine, S. L. Xiao - Qaidam	1.186/16	7.85	7.99	0.15	0.36	0.08	10.45	4.38	0.11	23.53	3.2	23.8	73.0	Halite	Ulexite	9 years
Z-Y	Surface Brine, L. Zhacang Caka	1.154/17	7.74	3.36	0.84	0.61	0.02	4.68	3.69	0.12	13.36	14.39	33.63	51.98	Mirabilite + Halite	Ulexite	12 years
D-12	Salt - Pool Brine, S. L. Da - Qaidam	1.246/15	7.15	5.69	0.79	2.18	0.02	13.98	2.77	0.179	25.61	7.81	69.53	22.66	halite	kumakovite	5 years
D-13	do.	1.290/15.5	6.69	2.78	1.37	4.33	0	13.08	6.88	0.27	28.71	6.36	66.67	26.97	halite	indente	5 years
D-14	do.	1.301/16	6.43	1.09	1.91	5.94	-	17.44	4.47	1.13	31.98	7.62	77.46	14.92	epsomite	indente	5 years
D-20	do.	1.366/8.6	5.04	tr.	0.11	8.92	-	22.22	2.79	2.18	36.9	0.36	92.14	7.50	late polash	MgO · 3B ₂ O ₃ · 7H ₂ O + 2MgO · 2B ₂ O ₃ · MgCl ₂ · 14H ₂ O	3-4 months
D-21	do.	1.390/23	4.99	tr.	0.09	10.02	-	24.73	3.67	2.19	41.4	0.26	91.20	8.54	bischofite	do.	3-4 months
Z-17	Concentrated Brine, S. L. Zhacang - Caka	1.3629/25	5.5	tr.	2.02	6.41	0	8.58	8.15	2.97	28.71	6.87	70.40	22.73	syvite	Indente + 2MgO · 2B ₂ O ₃ · MgCl ₂ · 14H ₂ O	3-4 months
Z-1	do.	1.3593/25	-	tr.	2.25	6.01	0	8.11	9.21	2.58	28.61	6.81	66.34	25.85	syvite	do.	3-4 months
D-20-1	D-20 precipitated borate	-	4.26	0.17	0.08	8.70	0	23.97	2.35	0.77	35.87	0.27	93.35	6.38	late polash	do. D-20	continue to crystallize
D-21-1	D-21 precipitated borate	-	4.10	0.26	0.05	8.91	0	25.03	1.90	0.77	36.93	0.16	94.27	5.12	bischofite	do. D-21	continue to crystallize
QE-E	Concent. brine, L. Qinghai	1.350	6.52	1.11	2.32	6.28	-	16.02	7.36	0.698	33.10	8.11	70.8	21.06	Carnallite	2MgO · 2B ₂ O ₃ · MgCl ₂ · 14H ₂ O	1-month
QFE-5	Do.	n. d.	5.89	0.34	0.47	7.94	-	3.76	20.49	0.529	33.60	1.60	87.93	10.47	Bischofite	2MgO · 2B ₂ O ₃ · MgCl ₂ · 14H ₂ O	1-month

The Qinghai - Xizang (Tibet) plateau of China is an important distributive area of the saline - lake borate deposits similar to that in South America. As for the formation of boron deposits, the boron source is mainly geothermal water (hot - spring water), which contains 26.07 ppm boron in average and 484.7 ppm maximum, and being controlled by the deep - big - faults of Bangonghu - Nujiang and South Side of Qilian Mts. etc. The secondary source is the acid magma rocks of different geological ages. They contain 62ppm - over 630ppm boron and are mainly distributed in the surrounding mountains of those lake basins. In this way, it leads to the formation of B-rich saline lakes and boron - ore deposits

in this area.

The California of United States is also an important distributive area of boron ore deposits in the world, such as Searls Lake, Boron Deposit and Death Valley etc. The geothermal water (hot spring) and volcano rocks are all the boron source. Especially, the volcano activities were very strong (basalt and tuff, widely) during the sedimentation of borate deposits at that age. For example, in the Death Valley, the Tertiary volcanoclastic rocks contain 50 - 700 ppm boron and the hot springs about 3.98 - 251 ppm boron (the maximum up to 2000ppm). These sources are very important for forming the big - type boron ore deposits in this area.

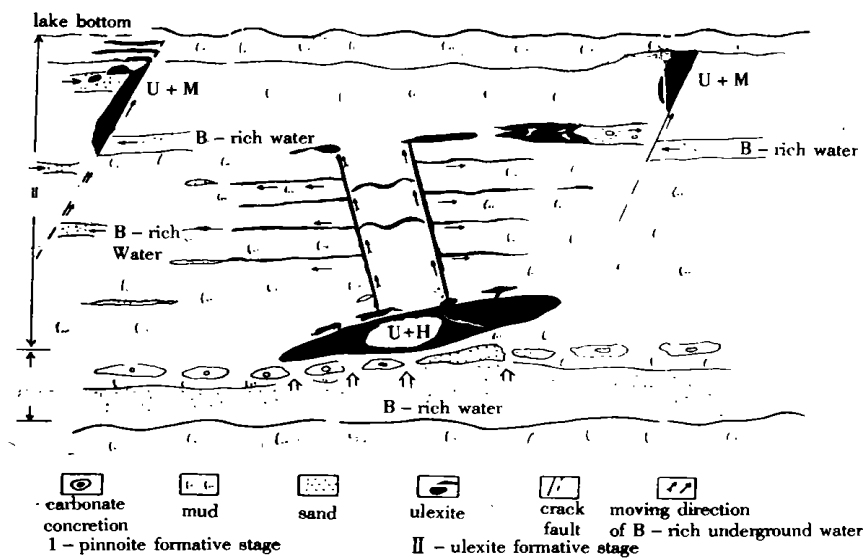


Fig.6 Schematic diagram of the formative process of borate in Xiao - Qaidam lake

The borate deposit of Turkey is the largest for the reserves of borate minerals in the world. In the Tertiary B-bearing basin, the volcano rocks (neutral - acid) formed during the borate precipitation are widespread and the important boron source for the boron mine formation in this area. It is very similar to the Boron Deposit in the California of United States.

In South America, the borate deposits lie in the high Andes in Argentina, Bolivia, Chile and Peru and consist of two genetical types of spring and playa de-

posits, which mainly make up of ulexite and borax. It is also an important area of borate deposits in the world and similar to those in the Qinghai - Xizang (Tibet) Plateau in China. According to some information, the springs are the main boron source in this area. For example, in Argentina the boron content of spring water is 24.79ppm - 78.53ppm, the maximum up to 512.59 ppm, etc.

Besides the above mentioned, the other borate deposits occurred in old salt deposits are mainly distributed in the Permian salt deposits of Europe, such

as Inder Potash Deposit, Stassfurt Potash Deposit etc. The former mainly consists of szaibelyite, hydroboracite, colemanite, ulexite and priceite etc, the later consists of boracite, inyoite, szaibelyite and hydroboracite etc. These boron deposits generally occur in the carnallite and bischofite—carnallite zones. As for the boron source for these deposits, it should be derived from the seawater at that time when those potash deposits were formed.

From the above, it may be seen that the boron source especially for the large—scale borate deposit in the continental basins should be derived from geothermal water and volcanic rocks. In fact, they depend on the deep magma activity. These basins also correspond to the tectonic—volcanic activating belt on the continental crust of the foreland area of underthrusting plate, such as high Andes, Qinghai—Tibet Plateau etc.

2 Origin of Borate Deposits

According to the above experimental results and the occurrences of borate deposits in nature, we will further discuss the origin as follows:

1) Borate deposits were formed in two kinds of B—rich water—bodies: carbonate and sulphate types

a. Carbonate (soda) type

At present, we have known that borax deposit is distributed in such a carbonate—type water—body (saline lake), such as the Searls Lake, Banguo—co Lake, Guojialin (Dujiali) Lake and Zabuye—Caka Lake etc. It should be also formed in the water—body, the freezing experimental result (5°C — -15°C) that obtained borax, natron and mirabilite (Table 4, Za—f) from the Zabuye—Caka Intercrystalline brine has proved this point. Glushvitski and Flerinskaya obtained borax, mirabilite, nahcolite and halite based on the research of the system Na/Cl , SO_4 , HCO_3 , B_4O_7 at 0°C (the liquid phase: NaCl —25.23%, Na_2SO_4 —1.32%, NaHCO_3 —0.32% and $\text{Na}_2\text{B}_4\text{O}_7$ —0.47%wt.) (Sdanovskiet al., 1954). It

also explains that borax deposit is formed in the water—body. In this way, the Kirka and Boron Deposits should be also formed in the carbonate—type water—body. The carbonate—type water—body may be spring water or general lake—water, and belongs to alkaline water ($\text{pH}=8.6-10.1$).

b. Sulphate type

It is a kind of water—body widespread for the formation of borate deposits, such as the B—rich hot springs and saline lakes in South America and on the Qinghai—Xizang Plateau of China. The borate deposits mainly consist of ulexite and Mg—borates, and they are distributed and formed in the sulphate—type water—body. For examples, ulexite is the main ore of many spring deposits and salt—lake deposits in South America and on the Qinghai—Xizang (Tibet) Plateau of China, such as the Rio Alumbrio deposits, Salars of Olaroz, Rincon, Pocitos and Centenario in Argentina, as well as the Da—and Xiao—Qaidam Lades (China), etc., and the Mg—borates of pinnoite, inderite and kurnakovite and so forth are also the main ore of some salt lake deposits in China, such as Da—and Xiao—Qaidam Lakes, Zhacang—Caka salt Lake etc. The old marine basins like the Permian potash deposits in Russia and Germany also belong to the sulphate—type water—body, and the Mg—borates of boracite, szaibelyite etc. in the Inder Potash Deposit and Stassfurt Potash Deposit ought to be formed in such a water—body as well.

The above experimental results have proved that these borates and boron deposits were formed in the sulphate—type water—body (Table 3, 4, 5) and at the same time reveal that they formed at the different concentrating stages of that water—body, namely, from Ca—Mg carbonate to bischofite separating stages (Fig. 2, 3). It will correct the point of that borate formed in the final stage of seawater concentration.

2) Precipitation of the borate deposits (except borax deposit) requires a rather stable environment, i.e. stable equilibrium condition.

It has been proved by the results of our experiments (Table 3—5), in which the samples were stored

for a certain period (3 months to 12 years) and the borates were just separated, among which the longest period was 12 years, secondary 9 years for ulexite precipitated from the surface brines of L. Zhacang - Caka and L. Xiao - Qaidam (Fig. 4). However, the precipitation of all borates is far later in time than that of other salt minerals, such as ulexite later mirabilite or halite etc.

In nature, such a stable environment mainly exists in the standing water of deeplake and in the subsurface intercrystal brine, void - water and fracture - water. The former is like the thick - bedded Kurnakovite deposits on the lakeshore terrace of Zhacang Caka Lake etc.; the later is like the ulexite deposits occurred with lentiform, nodules or vein - shape in Da - and Xiao - Qaidam Lakes (Fig. 4) and in the other salars of South America, and they are obviously secondary later in age than the overlying sediments (Fig. 5).

According to the above physico - chemical and geological conditions, the borates and borate deposits might be original and also secondary. The former often constitute the large - scale bedded ore deposit, such as Kirk Deposit (Turkey), Boron Deposit (U. S. A.) and so on.

3) Mixing action between various water - bodies is favorable to the formation of borate deposits

It has been proved by the above diluting experimental results. Thereby, at the inlet regions of stream and hot springs and the spring seepage zone on lakeshore or bottom, the borate deposits are distributed widely such as the boron mine area in the east of Da - Qaidam Salt Lake etc.

4) Low temperature is favorable to the formation of borate deposits.

The above freezing experiments (Table 4) and boron ore deposits in paragenesis with mirabilite all proved this point, such as the Xiao - Qaidam ore deposit etc.

5) Precipitation of the borate deposits is also controlled by the chemical composition of two kinds of B - rich water - bodies for sulphate and carbonate

types.

For example, the Mg - borate deposition lies in sulphate - type water - body and is controlled by the related contents of B_2O_3 , Mg, total salt and pH value, and the correlation equations is shown as follows:

$$a. Y = 0.3641X - 0.0575X + 0.00238X^2 \quad (Y = B_2O_3, X = \text{total salt});$$

$$b. Y = 1.2698 + 4.3276X \quad (Y = Mg, X = B_2O_3);$$

$$c. Y = 0.3641 - 0.0575X + 0.0024X^2 \quad (Y = B_2O_3, X = pH).$$

The correlation coefficients are 0.7563, 0.904 and -0.7563, respectively. These explain that both them have closely association during the course of borate separation.

6) Besides the above mentioned, the formation of the borate deposits (especially large - scale industrial resources) still requires a long - term ore - loading processes for the continuous migration and accumulation of boron substance derived from various water - bodies.

As for the original lacustrine deposit, its formation needs the unceasing supplying lake - basin of boron substance derived from surrounding B - rich water - bodies (hot - spring, spring, stream and river), and so many Boron - bearing sedimentary cycles are formed, such as Boron Deposit etc. As for the secondary borate deposit, its formation also requires a long - term ore - loading processes derived from the strong B - rich underground - water activities accompanied with tectonic - fault ones, such as in the Xiao Qaidam Lake, the ore - forming process includes two stages: (1) Ca - Mg carbonate - pinnoit formation and followed by (2) mirabilite - halite - ulexite formation (Fig. 3), the later has been proved by the boron isotopic composition of the mine water and ulexite. In which, the ratio between them ($^{11}B/^{10}B(mw)/^{11}B/^{10}B(u) = 1.004 - 1.006$) is consistent with the fractionation coefficient (1.003 - 1.007) of boron isotope for the borate precipitation (Sun, 1990). In fact, in many deposits, the two kinds of ore - forming processes often coexist and so the original

ore — body is also accompanied with secondary one.

CONCLUSION

From the above mentioned, it may be seen that the Origin of borate deposits under the condition of hypergenesis is complicated. It not only needs the enrichment boron source and favorable formative conditions, but also the long — term ore — loading processes.

1. Boron sources for the formation of borate deposits mainly have two kinds: geothermal activity and volcanic rocks. As to salt — lake and spring borate deposits on the Qinghai — Xizang (Tibet) Plateau in China and high Andes in South America, the main source is geothermal activity (hot — springs). As to Tertiary lacustrine boron deposits in Turkey and in California of United States, the volcanic activity and rocks are the important sources. However, as for the Permian boron deposits in Russia and Europe, the boron source should be old seawater.

2. Borate deposits can be formed in two kinds of B — rich water — bodies: carbonate and sulphate types (i. e. aqueo — salt equilibrium systems of $\text{Na}^+/\text{Cl}^-, \text{SO}_4^{2-}, \text{HCO}_3^-, \text{CO}_3^{2-} \cdot \text{H}_2\text{O}$ and $\text{Na}^+, \text{K}^+, \text{Mg}^{2+}/\text{Cl}^-, \text{SO}_4^{2-} \cdot \text{H}_2\text{O}$). At the same time, they might be also formed in these water — bodies of different concentration and various salt — separating stages. The borax deposit was formed in the carbonate — type water — body, and the ulexite and Mg — borate deposits in the sulphate — type one. In nature, some boron ore deposits contain many kinds of borate minerals, which results from the complicated and changeable water — bodies in chemical composition.

3. Generally, the formation of borate (besides borax) deposits lies at the stable equilibrium condition, not at the metastable equilibrium one. It has been proved by a lot of simulating experiments of ours.

4. Low — temperature condition is extremely favourable to the borate and boron ore deposition in

B — rich water — bodies. It has been proved by their paragenetic mineral groups and the above experimental results.

5. Precipitation of Mg — borates and their deposits is closely related to B — content, Mg — content, pH value and total salinity of the sulphate — type water — bodies.

6. In nature, the origin of borate deposits results from many — factor action and also underwent the complicated ore — forming processes. Through the research results, We illustrate the formation of the continental borate deposits, and also reveal the origin of the marine boron deposits.

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表生作用条件下硼酸盐矿床的形成问题

孙大鹏¹, 高章洪¹, 马育华¹, 蔡克勤², 帅开业², 高建华²

(1. 中国科学院青海盐湖研究所, 青海 西宁 810008; 2. 中国地质大学(北京), 北京 100083)

摘要: 沉积硼酸盐矿床在自然界分布相当广泛, 主要见于南、北美和我国青藏高原的盐湖中、美国 and 土耳其某些第三纪沉积盆地中, 以及欧洲某些古代海相盐矿床中。为了研究其形成问题, 从 70 年代开始, 我们利用青藏高原盐湖卤水和泉水进行了许多模拟实验工作。从 40~50 个样品中获得了大量钠硼酸盐、钠钙硼酸盐、镁硼酸盐和含氯化镁的镁硼酸盐复盐。这对于阐明表生作用条件下硼酸盐矿床的形成是非常重要的。

实验和研究结果证明:

- 1)与地热和火山活动有关的水体是硼酸盐矿床形成的物质来源；
- 2)硼酸盐矿床可形成于 $\text{Na、K、Mg//Cl、SO}_4\cdot\text{H}_2\text{O}$ 和 $\text{Na、K//Cl、SO}_4\text{、HCO}_3\text{、CO}_3\cdot\text{H}_2\text{O}$ 不同水盐平衡体系的不同富硼水体中(盐度:1.27~41.4%, B_2O_3 含量:0.05~2.97%);
- 3)硼酸盐矿床通常形成于稳定平衡条件下,而不是介稳平衡条件下(蒸发过程中);
- 4)低温条件有利于硼酸盐自水体中析出;
- 5)硼酸盐矿床的形成与水体的化学类型、pH 值和硼含量有密切关系;
- 6)我们实验中所获的硼酸盐反映了天然硼酸盐矿床形成的原始条件。不仅揭示了大陆盐湖硼酸盐矿床的形成,也揭示了古代海相盐矿床硼酸盐的成因。

关键词:硼酸盐矿床;表生作用;形成