

Origin of Salts in Pond Waters of the Labyrinth in Southern Victoria Land, Antarctica: A Study on Lithium and Boron Abundances

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南極南ビクトリアランドのラビリンスにおける池水中の塩起因：
リチウムとほう素からの考察

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要旨：南極南ビクトリアランド・ドライバレー地域・ラビリンス (77°33'S, 160°50'E) の池水中の塩起因を明らかにするため、Li と B 含量を測定した。また、これらと比較するため、ドライバレー地域のバンダ湖、ドンファン池、フリクセル湖およびボニー湖ならびにベストフォールドヒルズのディープ湖とエース湖についても同様の測定を行った。ラビリンスの淡水および塩水中の Li および B の濃度および濃縮係数などより、池水の化学成分は海水や熱水起源ではなく、おもに風送塩に起因するものであることが明らかになった。これらのことはラビリンスの塩水池が風送塩を含む氷河水や雪の融水が凍結濃縮を繰り返すことによって形成されたとする考えを支持している。塩化物イオン含量の増加とともに B/Cl 比が減少することから、B は凍結過程で氷に移行し、蒸発によって徐々に揮発していくと考えられる。

Abstract: Lithium and boron contents in pond waters of the Labyrinth (77°33'S, 160°50'E) of the Dry Valleys region in Southern Victoria Land, Antarctica were determined to elucidate the origin of dissolved salts. Also Lakes Vanda, Fryxell and Bonney, and Don Juan Pond in the Dry Valleys region as well as Deep and Ace Lakes in the Vestfold Hills were studied for comparison. The contents and enrichment factors of Li and B in both freshwater and saline ponds in the Labyrinth reveal that major ionic components in the pond waters originate mainly from atmospheric salts, rather than from trapped seawater and/or hydrothermal waters. These results support that the saline pond waters in the Labyrinth can be formed by the successive concentration through evaporation of pond waters supplied from glacial ice and/or snow containing atmospheric salts. The decrease of B/Cl ratios with the increase of chloride ion contents implies strongly that B is transported into ice during freezing of pond water, then volatilizes gradually to the atmosphere under frigid conditions.

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1. Introduction

Since the International Geophysical Year (1957–1959), a large number of lakes and ponds are found in the Dry Valleys region of Southern Victoria Land, Antarctica. The compositions of the major ionic components in these waters are very complicated. Many ideas for the origins of salts in the waters have been presented by various investigators. TORII and YAMAGATA (1981) and TORII *et al.* (1981) have proposed a hypothesis that some saline lakes or ponds can be formed by the successive concentration of pond waters through evaporation and freezing under frigid conditions. Further, to verify this hypothesis, TORII *et al.* (1988) have investigated pond waters in the high elevated inland areas of the Upper Wright Valley, the Labyrinth where the possibility of trapping of seawater cannot be easily assumed. The origin of salts is discussed based on major ionic components and isotopic ratios for hydrogen and oxygen of the pond waters.

Seawater contains considerable amounts of Li (0.190 ppm) and B (4.35 ppm) (SEYFRIED *et al.*, 1984). Also it is well known that both elements are enriched in thermal water of high temperature. These suggest that Li and B can be used as good indicators to judge whether the chemical components of the pond waters in the Labyrinth are associated with seawater or with thermal water. However, little is known on abundances of Li and B in the Dry Valleys region including the Labyrinth. Here we report Li and B of pond waters in the Labyrinth to clarify the origin of salts and to know their behaviors under frigid conditions. Also some related water samples from the Dry Valleys region and Vestfold Hills were studied for comparison.

2. Experimental

2.1. Sampling site

The Labyrinth, an extensive ice-free area of about 30 km² with 5.5 km width and 7 km length, is situated near the terminus of the Wright Upper Glacier at the west end of the Wright Valley (Fig. 1). The altitude ranges from 600 to 1000 m above sea level. The basement rocks in the area consist mainly of dolerite covered with an extremely thin sediment layer (SELBY and WILSON, 1971). More than 60 ponds are found in depressions where meltwaters are supplied from glacier and/or snowdrift banks. Surprisingly, more than a half of them are saline ponds (TORII *et al.*, 1988).

2.2. Analyses

Water samples from the Labyrinth pond, meltstream and pond ice core were collected during the austral summers of 1976–1977 to 1985–1986. After drilling into the pond ice using a SIPRE ice auger or breaking down the ice with an ice axe, pond water samples were collected using a hand-operated siphon and/or directly with polyethylene bottles. Meltstream was directly taken with polyethylene bottles. Ice core was obtained using a SIPRE ice auger. The lithium content was determined by atomic absorption method (ABE and HAYASHI, 1979). Boron was quantified by a colorimetric method using azomethine-H (SCHUCKER *et al.*, 1975). Chloride ion contents were determined by the methods of IWASAKI *et al.* (1956) for low salinity and of DOMASK and KOBE (1952) for high salinity. To compare the geochemical features

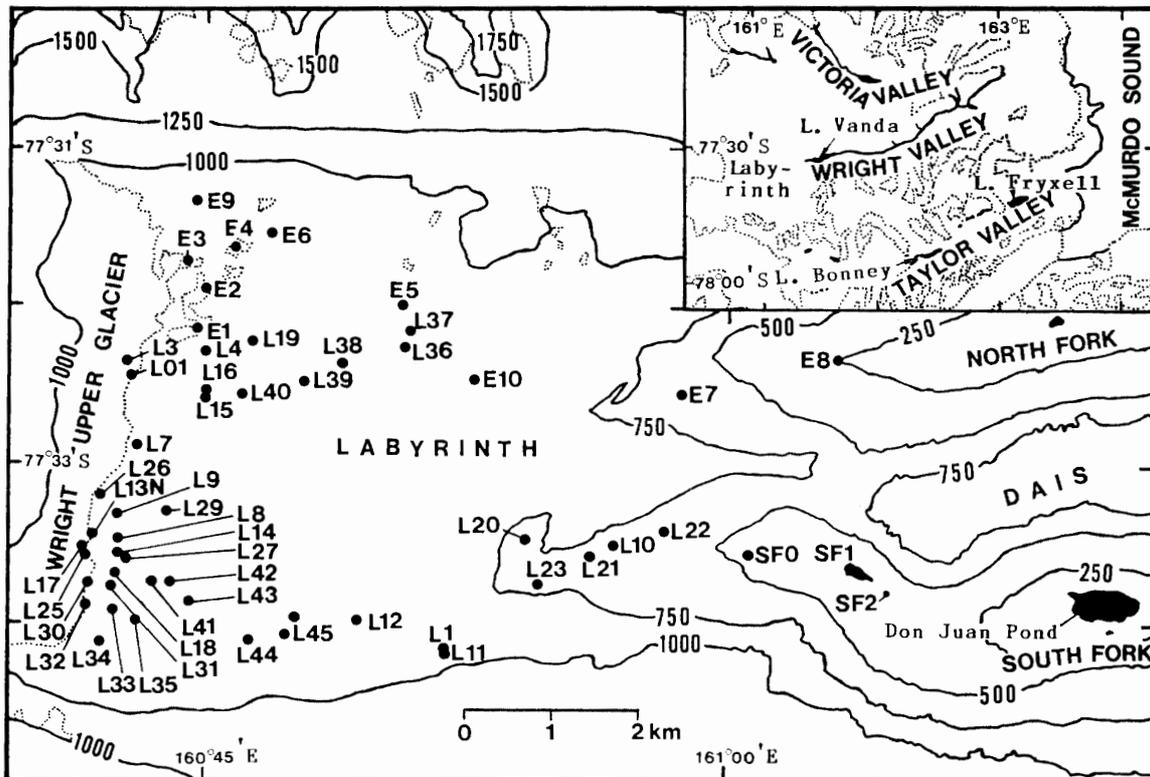


Fig. 1. Location of ponds in the Labyrinth.

of Li and B in the Labyrinth ponds, also their contents were determined for water samples from Lakes Fryxell, Bonney and Vanda and Don Juan Pond in the Dry Valleys region of Southern Victoria Land, Ross Sea, Deep and Ace Lakes in the Vestfold Hills located along the northeast coast of Prydz Bay, Princess Elizabeth Land ($68^{\circ}34'S$, $78^{\circ}11'E$).

A laboratory experiment was performed to elucidate the behavior of B in the concentration process of seawater under frigid conditions. Five beakers containing 100 ml seawater collected from Oshima Island, Tokyo were placed into a refrigerator at the temperature from -10 to $-15^{\circ}C$. The solution that remained unfrozen was separated from ice, and B and chloride ion contents were determined.

3. Results

The lithium and boron contents for 32 pond water, 2 meltstream and 8 pond ice core samples in the Labyrinth are shown in Table 1, and for water samples from the Dry Valleys lakes and pond (Lakes Fryxell, Bonney and Vanda, Don Juan Pond) and from the Vestfold Hills lakes (Deep and Ace Lakes) are shown in Table 2. The lithium contents in both fresh and saline pond waters, meltstream and ice core samples in the Labyrinth were all less than 0.02 mg/l, while those in the Dry Valleys lake and pond waters and Vestfold Hills lake waters ranged from 0.13 to 390 mg/l. The last-mentioned are generally much higher than that in seawater from the Ross Sea (0.15 mg/l, Table 2). Extremely high Li content was found in Don Juan Pond (390 mg/l).

The boron contents in the Labyrinth pond, meltstream and pond ice core samples

Table 1. Analytical results for pond waters in the Labyrinth.

Pond	Sampling date	Depth (cm)	Water temp. (°C)	Li (mg/l)	B (mg/l)	Cl (mg/l)	E_B^*	Note
L-0-1	21 Dec. '85	95	-2.8	nd	1.96	20400	0.418	Saline
L-0-2	23 Dec. '85	65	0.8	nd	0.27	3080	0.38	Saline
L-1	3 Jan. '77			nd	0.99	7580	0.57	Saline
L-4	14 Dec. '84		0.3	nd	4.17	37200	0.488	Saline
L-7	4 Jan. '83		0.7	nd	3.48	15780	0.959	Saline
L-7	16 Dec. '84		3.0	nd	8.59	38100	0.980	Saline
L-8	22 Dec. '85	Surface	4.2	nd	0.27	1040	1.1	Saline
L-9	22 Dec. '85	40	2.0	nd	0.96	7170	0.58	Saline
L-12-1	28 Dec. '83	Surface	3.0	nd	0.03	78.3	2	Fresh
L-13-S	22 Dec. '85	83	11.5	nd	0.67	1510	1.9	Saline
L-13-N	22 Dec. '85	74		nd	0.59	1230	2.1	Saline
L-14	5 Jan. '82	15	7.4	nd	2.52	10400	1.05	Saline
L-15	4 Jan. '82			nd	0.09	2903	0.1	Saline
L-16	24 Dec. '83	Surface	1.1	nd	0.11	169	2.8	Fresh
L-19	24 Dec. '83	Surface		nd	4.2	26700	0.68	Saline
L-20	27 Dec. '83	Surface	0.7	nd	0.06	93.6	3	Fresh
L-22-1	27 Dec. '83	Surface	2.3	nd	0.11	231	2.1	Fresh
L-26	27 Dec. '85	10	1.7	nd	0.07	134	2	Fresh
L-28	27 Dec. '85		-0.2	nd	0.25	743	1.5	Saline
L-29	27 Dec. '85	65	0.8	nd	0.05	53.6	4	Fresh
L-32	27 Dec. '85	20	0.0	nd	0.07	15.7	20	Fresh
L-35	27 Dec. '85	6	1.5	nd	2.79	13500	0.899	Saline
L-36	28 Dec. '85	5	0.0	nd	0.39	1500	1.1	Saline
L-37	28 Dec. '85	5	-1.2	nd	0.83	8570	0.42	Saline
L-38	28 Dec. '85	5	-0.4	nd	0.59	1430	1.8	Saline
L-40	28 Dec. '85	10	0.8	nd	0.10	103	4.2	Fresh
L-42	31 Dec. '85	5	-0.8	nd	2.44	5120	2.07	Saline
L-43	31 Dec. '85	5	-0.5	nd	0.17	66.7	11	Fresh
L-44	31 Dec. '85	20	-0.2	nd	0.16	10600	0.066	Saline
L-45	31 Dec. '85	10	-0.6	nd	0.35	1010	1.5	Saline
E-1	24 Dec. '85	79	1.0	nd	2.99	19100	0.68	Saline
E-7	17 Dec. '84			nd	0.03	48.1	3	Fresh
L-00	21 Dec. '85	0-50		nd	0.05	19.4	11	Ice core
L-00	21 Dec. '85	57-83		nd	0.05	11.1	20	Ice core
L-00	21 Dec. '85	83-100		nd	0.05	26.1	8	Ice core
L-00	21 Dec. '85	100-123		nd	0.03	27.5	5	Ice core
L-00	21 Dec. '85	123-152		nd	0.05	10.3	21	Ice core
L-00	21 Dec. '85	180-200		nd	0.05	28.2	8	Ice core
L-00	21 Dec. '85	222-236		nd	0.05	14.7	15	Ice core
L-00	21 Dec. '85	236-260		nd	0.05	12.7	17	Ice core
E-3-I	13 Dec. '84		0.0	nd	0.05	3.70	59	Inflow to E-3
E-3-I	24 Dec. '85		0.0	nd	0.27	392	3.0	Inflow to E-3

nd: Not detected.

* $E_B = (B/Cl)_{\text{sample}} / (B/Cl)_{\text{seawater}}$

Table 2. *Li and B contents of lake and pond waters in the Dry Valleys region and Vestfold Hills.*

Sample (depth, m)	Li (mg/l)	B (mg/l)	Cl (mg/l)	E_{Li}^*	E_B^{**}
Dry Valleys					
L. Fryxell (18.5 m)	0.13	3.18	3800	4.5	3.64
L. Bonney, west lobe (30 m)	5.1	24.1	88800	7.5	1.18
L. Bonney, east lobe (30 m)	8.8	44.9	168700	6.8	1.16
L. Vanda (69.5 m)	27	4.10	75930	47	0.235
Don Juan Pond	390	3.18	307800	166	0.0449
Vestfold Hills					
Deep L. (33 m)	1.58	40.5	157600	1.31	1.12
Ace L. (21 m)	0.15	5.01	23200	0.85	0.939
Ross Sea					
Near Scott Base	0.15	4.52	19660	1	1

* $E_{Li} = (Li/Cl)_{\text{sample}} / (Li/Cl)_{\text{seawater}}$

** $E_B = (B/Cl)_{\text{sample}} / (B/Cl)_{\text{seawater}}$

varied from 0.03 to 8.59 mg/l, which were generally considerably lower than that in seawater (4.52 mg/l), whereas those in the Dry Valleys lake and pond waters and the Vestfold Hills lake waters ranged from 3.18 to 44.9 mg/l. High B contents were found in the east and west lobes of Lake Bonney and Deep Lake (Tables 1 and 2).

4. Discussion

4.1. Lithium

Lithium abundances for natural waters are summarized by HEIER and BILLINGS (1969, Table 3). The Li contents for rain water and snow may be too low to be determined by usual analytical methods (FETH *et al.*, 1964). The Li contents of seawaters range from 0.15 to 0.19 ppm depending on the sampling locality (TAKAMATSU *et al.*, 1980; SEYFRIED *et al.*, 1984).

TAKAMATSU *et al.* (1980, 1983, 1986) reported the Li contents of thermal spring waters in Japan and indicated that Li is enriched in highly saline spring waters. They explained that the high Li contents of these saline waters are due to the hydrothermal reaction of rocks with salt solutions such as seawater and/or due to the dissolution of trapped salts containing Li. Thus the Li abundances vary largely with salt sources. Namely, the Li contents in pond waters supplied only by precipitation can be expected to be extremely low, while those in the water bodies influenced by hydrothermal activity as well as seawater should be high.

Table 3. *Statistics for Li in various waters (ppm) (HEIER and BILLINGS, 1969).*

	\bar{X}	S.D.	n	Median	Range
Precipitation	0.0				
River waters	0.023	0.082	56	0.01	0.001- 0.4
Seawater	0.190	—	—	—	—
Formation waters (brines)	26	26	134	19	0.04 -100
Hydrothermal waters	8.2	5.7	258	8.5	0.01 - 27

Here, the following enrichment factor for Li (E_{Li}) was used to discuss the behavior of Li in the Labyrinth ponds as well as related lakes and pond in the Dry Valleys region and Vestfold Hills.

$$E_{Li} = \frac{(Li/Cl)_{sample}}{(Li/Cl)_{seawater}}$$

The E_{Li} values for freshwater and saline ponds in the Labyrinth were all near zero even when some of their chloride ion contents were much higher than the seawater, whereas those for Deep and Ace Lakes were near unity (Fig. 2). The E_{Li} values for Lake Fryxell and the east and west lobes of Lake Bonney were considerably higher than unity. Extremely high E_{Li} values were observed in Don Juan Pond and Lake Vanda. There are four possible explanations of these Li distributions in the studied areas: salts originated from 1) trapped seawater, 2) hydrothermal water, 3) rock weathering, and 4) atmospheric salts.

The ratios of the major ionic components to chloride ion in Deep and Ace Lakes are similar to those in seawater, implying that the salts are derived from seawater (MCLEOD, 1964). Our E_{Li} values for these lakes are also similar to that for seawater, supporting the above explanation. Thus for these lakes, Li has originated mainly from trapped seawater.

Geochemical studies of secondary minerals suggested the occurrence of hydrothermal activity in the Don Juan Basin and around Lake Vanda (MORIKAWA *et al.*,

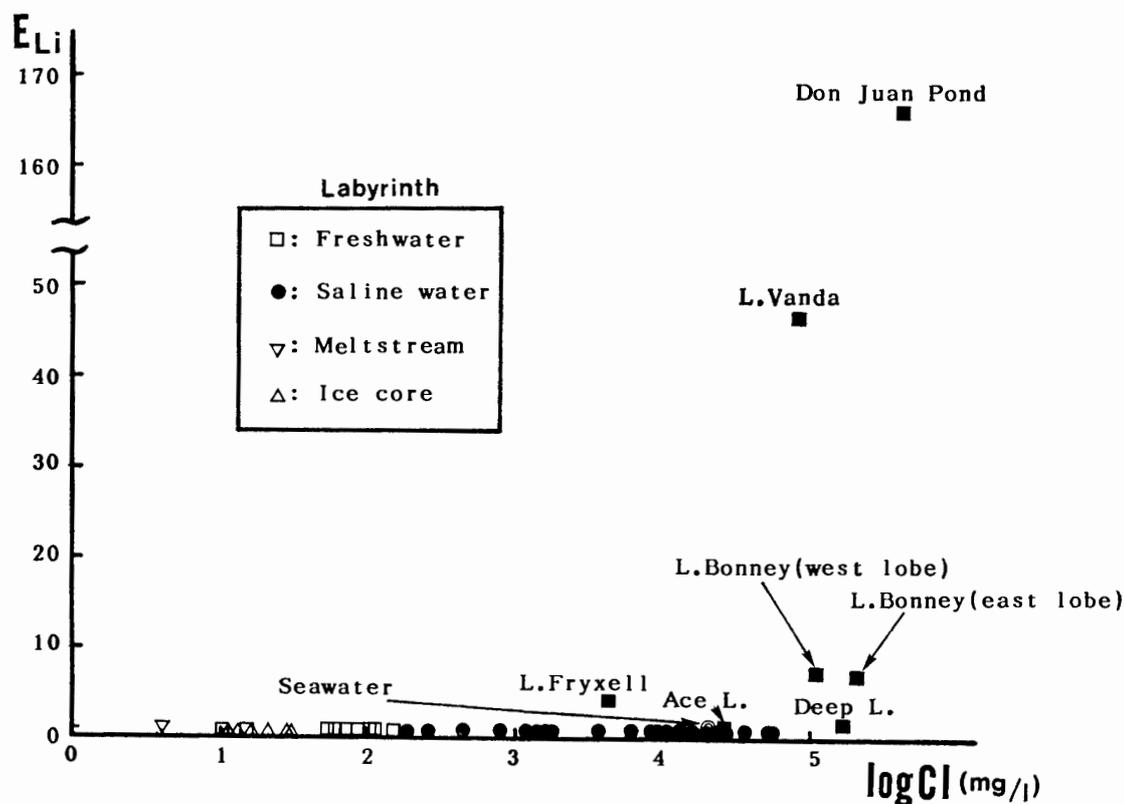


Fig. 2. Relationship between E_{Li} and $\log Cl$ of the water samples from the Labyrinth ponds and some related lakes and pond in the Dry Valleys region and Vestfold Hills.

1975; NISHIYAMA, 1977). KOGA (1977) studied mercury distributions in the surroundings of Lake Vanda and suggested the existence of thermal sources under the ground. The extremely high E_{Li} values of Lake Vanda and Don Juan Pond may be attributed to the influence of hydrothermal activity. It is known that Lakes Fryxell and Bonney are influenced by seawater (ANGINO *et al.*, 1962, 1965; KEYS, 1980). The relatively high E_{Li} values for these lakes seem to be due to the contribution of seawater, in addition to hydrothermal activity which is suggested by the presence of cinder cones in the Taylor Valley.

The very low E_{Li} values for the Labyrinth ponds strongly suggest that the origin of salts are fundamentally different from those in the saline waters in the Dry Valleys lakes and pond as well as the Vestfold Hills lakes studied so far. That is, the major ionic components in both freshwater and saline ponds in the Labyrinth originate mainly from atmospheric salts, other than from trapped seawater and hydrothermal waters. These results are consistent with those of the previous study reported by TORII *et al.* (1988). Also these results revealed that the contribution of rock weathering to the Li abundance in frigid conditions is negligible.

4.2. Boron

Numerous geochemical data for B in the natural waters have been accumulated. Boron is remarkably condensed in rain and snow and the gravimetric ratios of B to Cl range from several to some thousands times greater than that of seawater (SUGAWARA, 1948; MUTO, 1956; HANDA, 1969; SUPATASHVILI, 1977, Table 4). Therefore, if the pond waters in the Labyrinth are fed mainly by precipitations, the B/Cl ratios would be fairly high.

Table 4. Examples of boron contents and enrichment factors for precipitation in Japan and Indian Ocean.

	B (g/l)	Cl (mg/l)	E_B^*
SUGAWARA (1948) Nagoya	71-160	0.113-0.694	960-4600
MUTO (1956) Kiryu	20-150	0.38 - 2.91	54- 279
KAWAGUCHI (1958) Nagoya	2- 9.3	0.4 - 1.7	16- 64
SUPATASHVILI (1977) Indian Ocean	18- 57.0	2.6 -15.5	18- 52

$$* E_B = (B/Cl)_{\text{precipitation}} / (B/Cl)_{\text{seawater}}$$

Figure 3 shows the relationship between log Cl and E_B value (enrichment factor for B) for the Labyrinth pond waters, together with the Dry Valleys lakes and pond and Vestfold Hills lakes. The E_B values for the ice core sample, freshwater ponds and the meltstream waters into a saline pond (E-3) in the Labyrinth and Lake Fryxell were much higher than unity, but those in some saline ponds and Lake Vanda and Don Juan Pond were much lower than unity. The E_B values for the east and west lobes of Lake Bonney, and Deep and Ace Lakes were similar to that of seawater. The high E_B values in the freshwater ponds and glacial meltwaters in the Labyrinth can be explained by the contribution of atmospheric salts, since precipitation has high E_B values as noted above (Table 3).

Generally, the E_B values decreased gradually with the increase of chloride ion contents except for some lakes. This indicates the occurrence of some removal

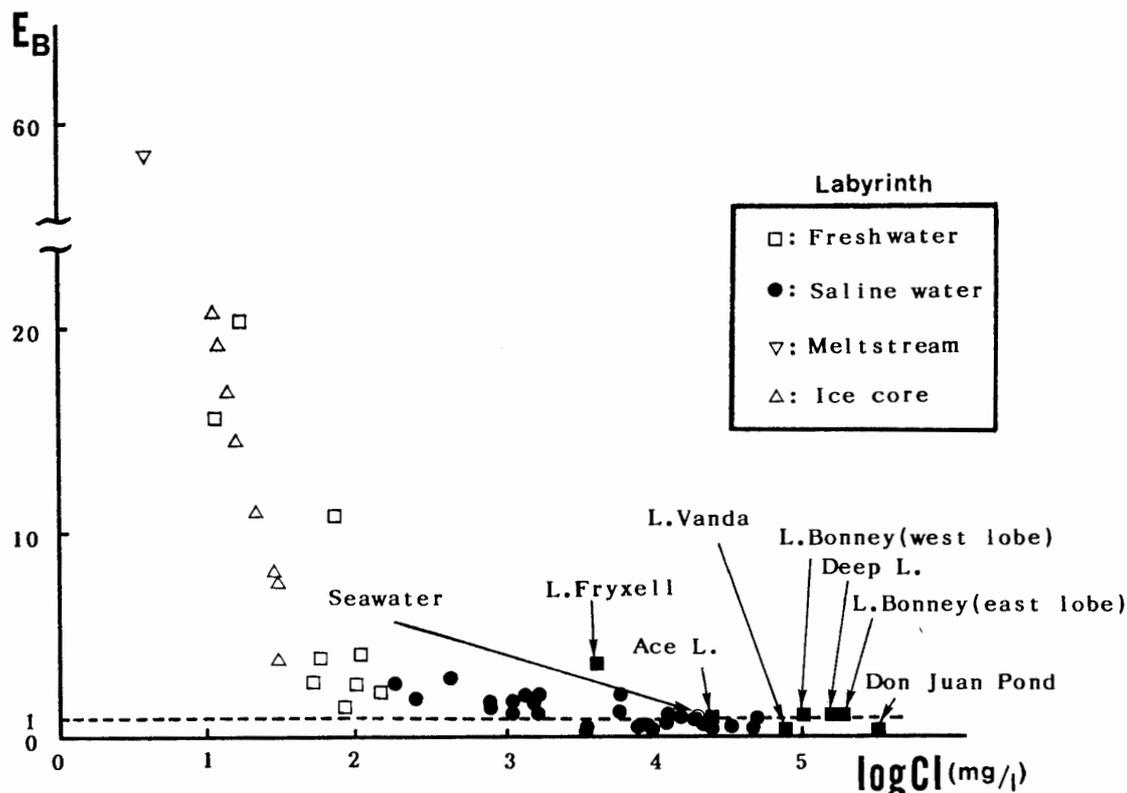


Fig. 3. Relationship between E_B and $\log Cl$ of the water samples from the Labyrinth ponds and some related lakes and pond in the Dry Valleys region and Vestfold Hills.

processes of B during the concentration of pond waters. It is possible that B migrated into ice during the freeze concentration of pond water. To clarify this hypothesis, the laboratory experiment was performed. It was found that the E_B values decreased with the increase of chloride ion contents during the freeze concentration of seawater (Fig. 4). These results suggest strongly that B migrates from pond water into ice. Also it is known that B is volatile in the natural conditions as evidenced by its high abundance in precipitation. Therefore, the distributions of B in the Labyrinth ponds can be explained as follows: Glacial and snow meltwaters containing atmospheric salts of high E_B values are pooled in freshwater ponds, and then the freezing and/or evaporation of pond waters form saline ponds accompanying the discrimination of B.

Various E_B values for the Dry Valleys lakes and pond, and Vestfold Hills Lakes studied so far are possibly attributed to the mixed effects of the evaporation of waters and the supply of precipitation, in addition to the difference of salt sources as discussed above.

5. Conclusions

The E_{Li} values in both fresh water and saline ponds in the Labyrinth were extremely low. The E_B values in fresh water ponds were all considerably higher than unity, while those in saline ponds were generally low. No evidence of trapped seawater and hydrothermal waters was indicated in the Labyrinth ponds. The origin of

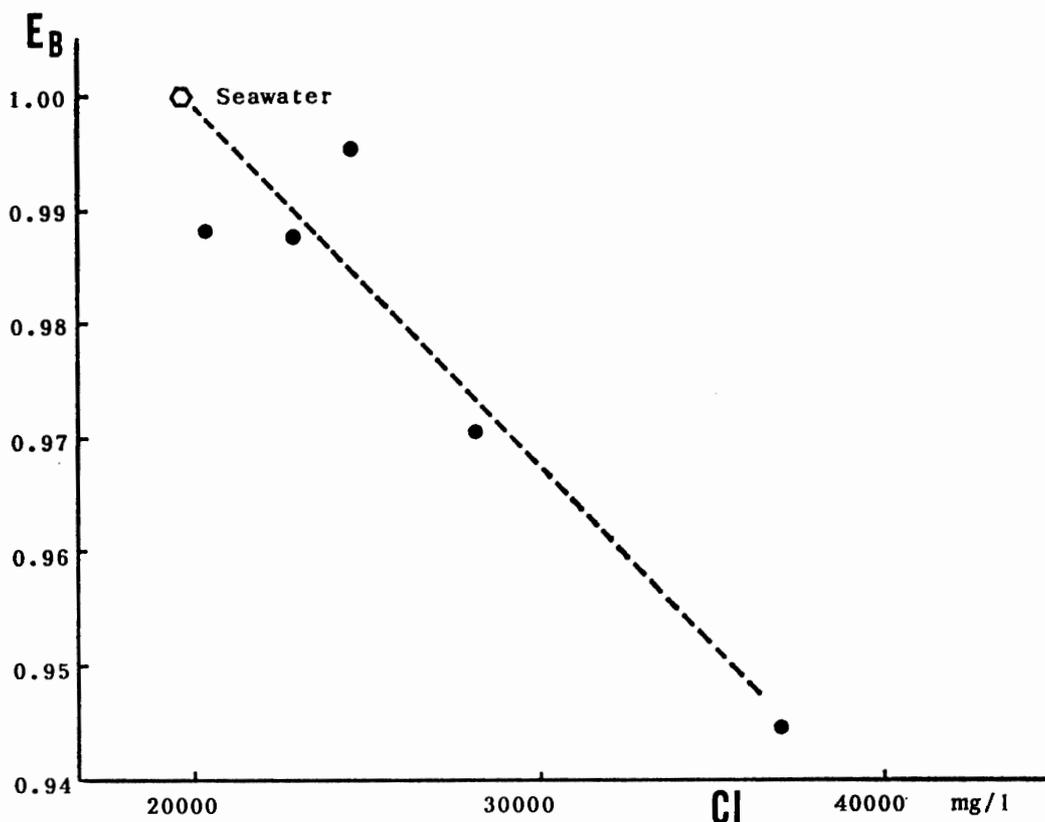


Fig. 4. Relationship between E_B and Cl content during the freeze concentration of seawater.

salts in the pond waters in the Labyrinth is concluded to be atmospheric salts. The gradual decrease of the E_B values with increasing chloride ion contents can be explained by the volatilization of B through the ice surface during freezing and evaporation processes under frigid conditions.

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