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ALKALI METAL CONSTRAINTS ON THE ORIGIN OF SALTS IN LAKES AND PONDS FROM THE McMURDO DRY VALLEYS, ANTARCTICA

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Abstract: Alkali metals in lake, pond, and ice samples of the McMurdo Dry Valleys in southern Victoria Land, Antarctica were studied to clarify the origins of dissolved salts and to estimate their evolutional history. The contents of Li, Rb and Cs largely varied ranging from 0.30 ppb to 390 ppm, 0.06 ppb to 514 ppb and 0.001 ppb to 90.9 ppb, respectively. The low rare alkali metal contents with high Ef_m [$Ef_m = (m/Cl)_s/(m/Cl)_{sw}$, m; alkali metal, s; sample, sw; seawater] values of the pond waters and ice samples in the Labyrinth imply that dissolved salts are mainly derived from atmospheric fallout. The decrease of Ef_m values with increasing Cl content of the Labyrinth pond waters suggests that rare alkali metals are removed from waters during freeze and evaporative concentrations. The bottom waters of Lakes Fryxell and Bonney may originate from trapped seawater influenced by water-rock interaction. The extremely high Ef_m values (especially the Ef_{Li}, Ef_{Cs} values) of Don Juan Pond water and the bottom water in Lake Vanda can be explained by the contribution of deep ground waters.

1. Introduction

The McMurdo Dry Valleys of southern Victoria Land, the largest ice-free area in Antarctica, is situated west of McMurdo Sound. The salt origin of lake and pond waters in this region have been investigated for nearly 30 years from a geochemical viewpoint. Many possible salt sources have been proposed: (1) trapped seawater (ANGINO and ARMITAGE, 1963; ANGINO *et al*., 1964; CRAIG, 1966), (2) atmospheric fallout (TORII *et al*., 1989), (3) rock weathering (HENDY *et al*., 1977; GREEN and CANFIELD, 1984), (4) ground water (GREEN and CANFIELD, 1984; TOMIYAMA and KITANO, 1985) and (5) hydrothermal waters (NISHIYAMA, 1975; KOGA, 1977).

As some major ions may be removed as deposits (halite, thenardite, gypsum, mirabilite and/or clay minerals, etc.) in the concentration processes of lake and pond waters, the discussion of the salt origin and alteration processes of the salt composition of waters has been complicated and debate is still continuing.

By using the minor and/or trace elements, the salt origin of Antarctic saline lakes has also been discussed. MASUDA *et al.* (1984) concluded that the salts of Antarctic lake and pond waters have been derived mostly from aerosol particles. TAKAMATSU *et al.* (1988) suggested from Boron content that dissolved salts in both freshwater and saline ponds of the Labyrinth originate mainly from atmospheric fallout. Moreover, TAKAMATSU *et al.* (1993) inferred that some of the salts in saline lakes having high lithium content are derived from water-rock interaction influenced by hydrothermal activity. Here we report mainly rare alkali metals (Li, Rb and Cs) in lake and pond waters of the McMurdo Dry Valleys to elucidate the origin of dissolved salts, and to estimate their evolutional history.

2. Experimental

Water samples of lakes and ponds from the Wright and Taylor Valleys in the McMurdo Dry Valleys were collected during the austral summers of 1974–1987 (Fig. 1). After drilling into lake and pond ice using a SIPRE ice auger or cutting into the ice with an ice axe, water samples were collected using a Kitahara-type water sampler (1 L) or directly with polyethylene bottles. Ice samples were obtained from a frozen pond in the Labyrinth and the Upper Wright Glacier.

The contents of Na and K of water and ice samples were analyzed by flame atomic absorption spectrometry. The Cl content was determined by mercuric thiocyanate spectrophotometry (IWASAKI *et al.*, 1956) or ion chromatography for low salinity and sliver nitrate

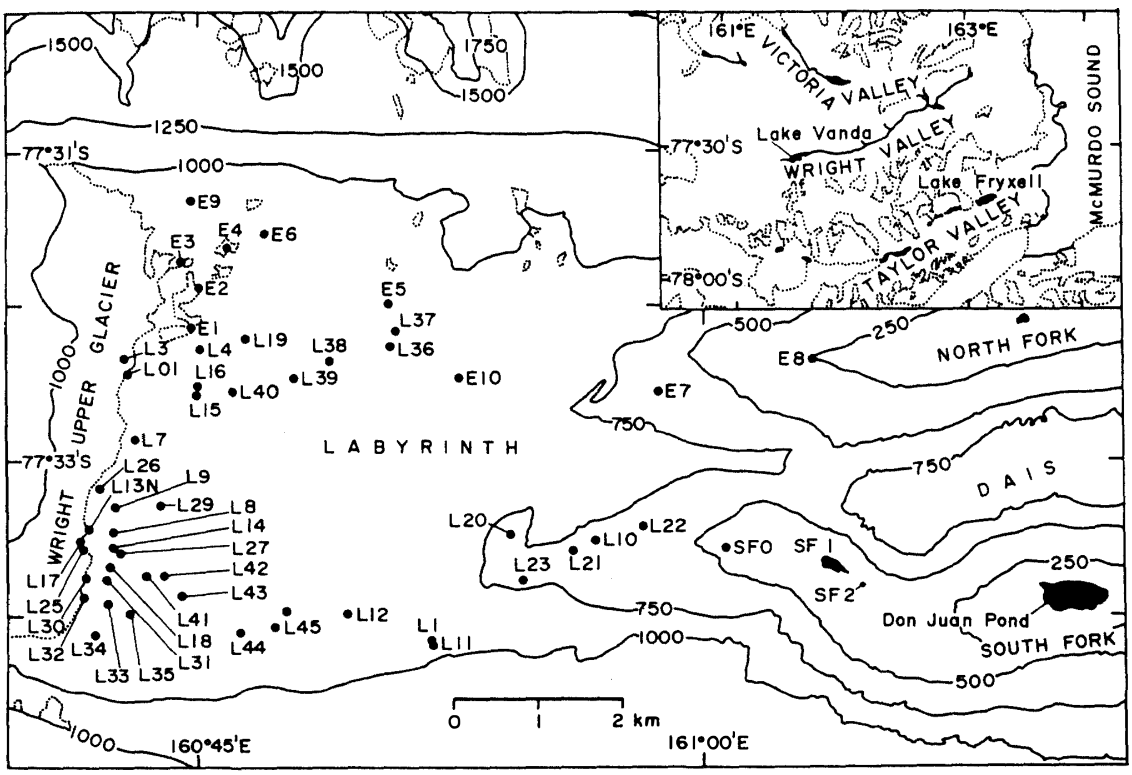

Fig. 1. Sampling locations of lake and pond waters in the McMurdo Dry Valleys of southern Victoria Land, Antarctica.

titration method (Mohr method) for high salinity. The quantitation of Li was done by flameless atomic absorption spectrometry (Kato and Takamatsu, 1989). The contents of Rb and Cs were determined by a Perkin-Elmer Elan 5000 Inductively Coupled Plasma Mass Spectrometer. The detection limits of Li, Rb and Cs were 0.02 ppb, 0.01 ppb and 0.001 ppb, respectively. The relative standard deviations for rare alkali metals were usually less than 10%, except for extremely low content.

3. Results and Discussion

3.1. *Alkali metal contents and Ef_m values*

Table 1 lists the analytical results of alkali metals and Cl contents. The rare alkali metal contents of the pond waters and ice samples (ice core of pond and the Wright Upper Glacier) in the Labyrinth were generally low, but those of Don Juan Pond water and the bottom water (69.5 m) in Lake Vanda were extremely high. The rare alkali metal contents of the bottom water (17.5 m) in Lake Fryxell were relatively high, whereas those of the bottom water (30.0 m) in the east lobe of Lake Bonney were very high.

The following enrichment factors for alkali metals are used to discuss the origins of salts and behaviors of alkali metals in lake and pond waters and ice samples:

$$Ef_m = (m/Cl)_{sample}/(m/Cl)_{seawater}, \qquad \text{m: alkali metals}$$

where the alkali metal contents of seawater are cited from reference data (Takamatsu *et al.*, 1988; Matsuo, 1989).

In the Labyrinth, the Ef_{Li}, Ef_{Rb} and Ef_{Cs} values of freshwater ponds and ice samples were very high, while those of saline ponds were generally low. The Ef_{Li} and Ef_{Cs} values of Don Juan Pond water and the bottom water in Lake Vanda were extremely high, whereas those in Lakes Fryxell and Bonney waters were close to unity ($LogEf_m$ values were zero).

Figures 2 and 3 show the relationships between $LogEf_m$ and LogCl of the lake and pond waters and ice samples of the McMurdo Dry Valleys. The $LogEf_m$ values (except for Na) in waters of the Labyrinth ponds were clearly different from those of Lakes Fryxell, Bonney, Vanda and Don Juan Pond. This implies that both salt origins and the concentration mechanisms of the salts in the waters are quite different from one another.

3.2. *Salt origin*

3.2.1. Labyrinth ponds

The $LogEf_{Na}$ values of the Labyrinth pond waters and ice samples were close to zero, indicating that the salts in these samples were mainly derived from atmospheric fallout containing sea salts as suggested by Torii *et al.* (1989). On the other hand, the $LogEf_m$ values for Li, K, Rb and Cs were very high. Takamatsu (1990) reported that the Ef_{Li} values of precipitations in Japan are very high. Thus the Ef_m values for alkali metals other than Na in atmospheric fallout would be expected to be very high, although very little is known about rare alkali metals in fallout in the world.

Interestingly, the $LogEf_m$ values for K, Li, Rb and Cs in the Labyrinth pond waters decreased linearly with LogCl (Figs. 2 and 3). This indicates that those alkali metals were removed from the pond waters by some mechanism during the freeze concentration.

Table 1. Alkali metal contents of lakes, ponds, and ice samples of McMurdo Dry Valleys.

Locality	Cl/ppm	Na/ppm	K/ppm	Li/ppb	Rb/ppb	Cs/ppb
Labyrinth pond						
L-0-1	20400	11200	52.3	39.0	9.59	<0.001
L-0-2	3080	1710	9.22	16.0	2.75	<0.001
L-7	5360	2920	32.0	6.0	5.74	0.020
L-7	38100	17400	6.34	35.0	14.5	0.200
L-8	1040	587	6.34	2.30	0.75	0.019
L-10	140	66.0	1.70	0.50	0.23	0.003
L-12-1	78.3	60.3	1.30	1.50	0.24	0.008
L-13-S	1510	1290	13.6	8.30	1.07	0.034
L-22-1	231	120	2.00	0.90	0.31	0.006
L-27	941	753	6.00	5.40	0.61	0.004
L-28	743	542	4.87	3.90	0.70	0.021
L-29	53.6	38.8	0.96	1.62	0.12	0.005
L-32	15.7	12.6	2.80	2.20	0.16	0.004
L-33	8.94	9.17	1.03	0.30	0.066	0.001
L-35	13500	8650	55.7	28.0	6.92	0.102
L-37	8570	4790	32.2	19.0	3.05	<0.001
L-38	1430	1010	8.70	9.50	1.16	0.098
L-39	5140	3070	26.0	8.70	3.00	<0.001
L-40	103	89.5	1.62	1.20	0.44	0.016
Lake Fryxell						
5 m	80.0	76.0	9.10	7.16	2.34	0.004
17.5 m	3830	2680	193	110	25.5	0.040
Lake Bonney						
East lobe 5 m	647	343	17.9	36.3	4.03	0.017
East lobe 30 m	142900	40500	2580	8800	346	2.12
West lobe 5 m	718	378	16.9	43.1	3.60	0.084
West lobe 30 m	86080	38500	1350	5100	189	0.700
Lake Vanda						
5 m	292	56.6	16.3	145	5.34	0.373
69.5 m	70300	5860	609	27000	173	5.40
Don Juan Pond	232300	4270	186	390000	514	90.9
Pond ice						
L-00-2	11.1	10.0	0.14	1.30	0.10	0.002
L-00-3	26.1	23.7	0.29	1.20	0.090	0.003
L-00-6	28.2	12.2	0.35	1.30	0.11	0.003
L-00-7	14.7	4.54	0.25	0.86	0.068	0.006
Glacier ice						
WUG-1	0.48	0.20	0.08	0.87	0.081	<0.001
WUG-4	0.46	0.10	0.03	0.043	0.015	0.002
WUG-5	0.20	0.05	0.02	0.093	0.030	0.001
WUG-8	0.40	0.21	0.09	0.30	0.13	<0.001
WUG-10	0.98	0.38	0.13	2.63	0.054	<0.001

WUG: Wright Upper Glacier.

There are three possible explanations: (1) deposition as salts, (2) relative enrichment to Cl in pond ice, and (3) interaction with clay minerals.

Salt deposition of rare alkali metals should not occur in such a low content range, even at low temperatures. A freeze concentration experiment using seawater revealed that Li was enriched in the ice phase (TAKAMATSU *et al*., 1993). Thus, it is likely that rare

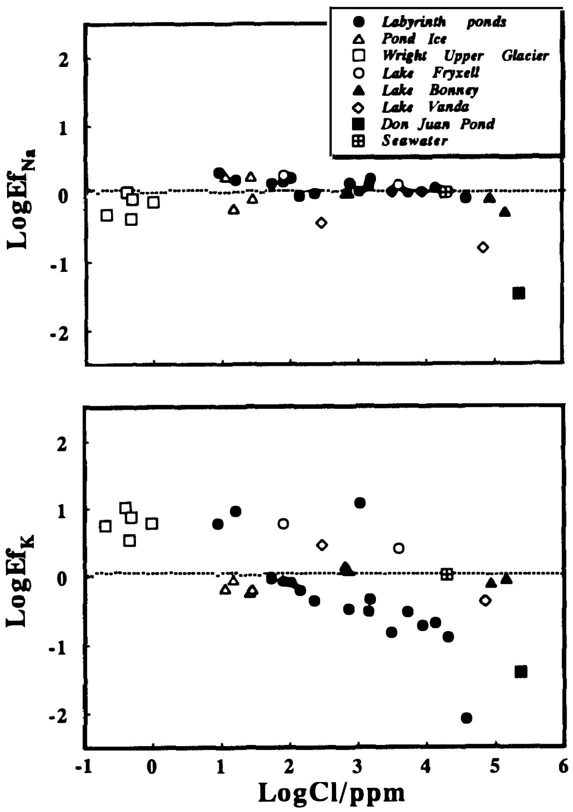

Fig. 2. Relationships between LogCl and $LogEf_m$ values for Na and K of lake and pond waters and ice samples in the McMurdo Dry Valleys.

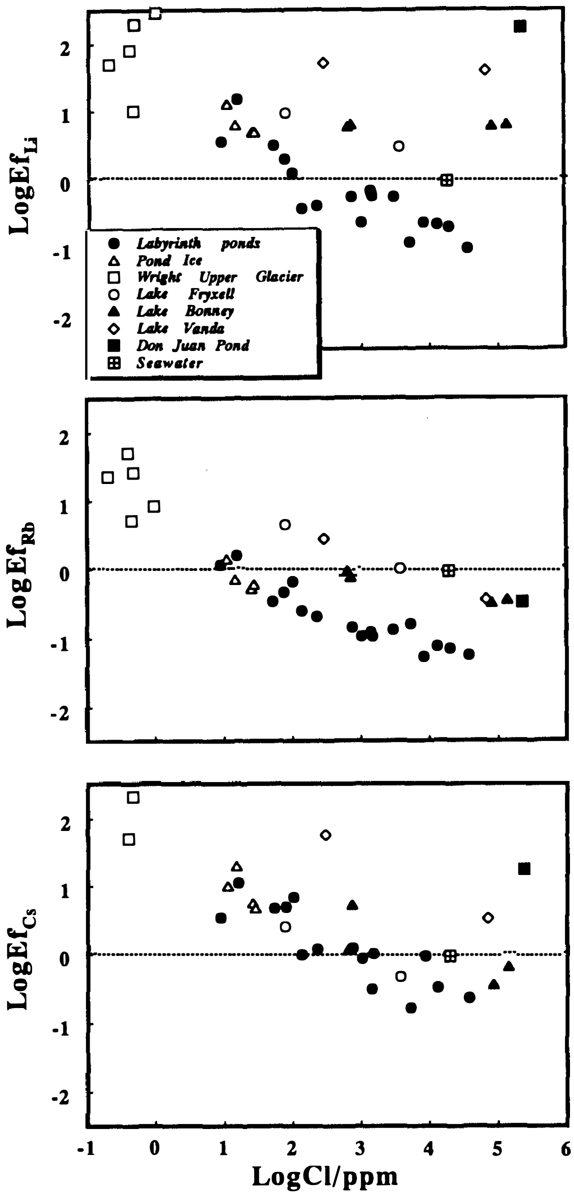

Fig. 3. Relationships between LogCl and $LogEf_m$ values for Li, Rb and Cs of lake and pond waters and ice samples in the McMurdo Dry Valleys.

alkali metals migrate into the ice phase during freeze concentration in the Labyrinth ponds. Also, the rare alkali metals may interact with clay minerals (uptake, adsorption, etc.). Further studies are needed to clarify the interaction between alkali metals and clay minerals.

3.2.2. Lakes Fryxell and Bonney

The $LogEf_m$ values for Na, K, Rb and Cs of bottom waters in Lakes Fryxell and Bonney were almost zero (Figs. 2 and 3). Major ionic components in the bottom water of Lake Fryxell water are generally similar to those in seawater, but their contents are about 1/5 of seawater (TORII *et al.*, 1975). Thus, the dissolved salts in the lake are believed to be trapped seawater. In the austral summer, meltwaters from Canada and Commonwealth Glaciers and local snow which contain atmospheric fallout and/or chemical weathering products contribute to the lake and dilute the trapped seawater (GREEN *et al.*, 1988). However, the very high Log Ef_{Li} values in the bottom water in the lake cannot be explained by the contribution of seawater and meltwater. Hence saline water-rock interaction may have occurred in the lake basin (TAKAMATSU *et al.*, 1993).

Several hypotheses concerning the salt origin of Lake Bonney have been proposed: trapped seawater (ANGINO and ARMITAGE, 1963; MORIKAWA *et al.*, 1975), chemical weathering (HENDY *et al.*, 1977), ground water (WEAND *et al.*, 1975), etc. MATSUBAYA *et al.* (1979) proposed a genetic mechanism of two lobes of Lake Bonney using isotopic water data. It is difficult to clarify the complicated evolutional history of Lake Bonney only by alkali metal data. However, the appreciably higher $LogEf_{Li}$ values than zero of Lake Bonney can be explained by the contribution of the salts derived from the saline water-rock interaction during the formation of the lakes (TAKAMATSU *et al.*, 1993).

3.2.3. Don Juan Pond and Lake Vanda

It is well known that Don Juan Pond water and the bottom water of Lake Vanda contain a large amount of salts with predominance of Ca and Cl (TORII and YAMAGATA, 1981). Thus their $LogEf_{Na}$ values were exceptionally low (Figs. 2 and 3). On the other hand, the $LogEf_{m}$ values for Li and Cs of Don Juan Pond water and the bottom water of Lake Vanda were much higher than zero, indicating that the source of Li and Cs cannot be interpreted simply by the contribution of relict seawater, atmospheric fallout or chemical weathering of rock.

Basement rocks in the McMurdo Dry Valleys mainly consist of a pre-Ordovician metasedimentary sequence composed of schist, hornfels, and marble;a younger set of granite and granite gneiss intrusion;overlying Beacon Sandstones intruded by the Ferrar Dolerites (VOCKE and Hanson, 1981). TAKAMATSU (1990) showed, from the dissolution experiments on various rocks, that the high Li contents of saline spring waters in Japan are due to the hydrothermal reaction of rocks with salt solutions such as seawater. The dissolution experiments of dolerite and granite from the McMurdo Dry Valleys at 40°C showed that the dissolved rare alkali metals in NaCl solution were much higher than those in distilled water (TAKAMATSU *et al.*, unpublished). These results suggest that the rare alkali metals can be derived from rocks by interaction with deep underground water containing salts. CARLSON *et al.* (1989) concluded from the $^{36}Cl/Cl$ ratio that nearly 100% of the Cl in the Don Juan Pond water and the bottom water of Lake Vanda originated from deep ground water in the granitic basement rocks. It has been reported that the calcium chloride groundwater is formed through long term active water-rock interaction underground in the Matsushiro area in Japan (YOSHIOKA *et al.*, 1970). This is consistent with the fact that Li and Cs contents in the Don Juan Pond water and the bottom water of Lake Vanda were extremely high.

The $LogEf_{K}$ value of the Don Juan Pond water was extremely low, indicating that K was removed from the aquifer near the surface during the freeze concentration as KCl deposition and/or by the mineral reconstitution or reverse weathering reactions with K-poor aluminosilicate minerals (GREEN *et al.*, 1988). The low $LogEf_{Rb}$ value of the Don Juan Pond water (less than zero) may show that Rb was deposited on the bottom during the concentration processes. Further studies are needed to interpret the similarity of K and Rb behavior in the extremely high saline waters of Lake Vanda and Don Juan Pond.

4. Conclusions

The low rare alkali metal contents with high Ef_m values of the pond waters in the Labyrinth are explained mainly by the contribution of atmospheric fallout. The saline bottom waters of Lakes Fryxell and Bonney may originate from relict seawater modified by the water-rock interaction. The extremely high Li and Cs contents with high Ef_m values of the Don Juan Pond water and the bottom water of Lake Vanda imply that the chemical composition of dissolved salts is influenced by deep ground waters containing high Li and Cs derived from water-rock interaction.

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