

Chemical and Isotopic Characterization of Lakes in the Larsemann Hills, East Antarctica



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Abstract The ionic and isotopic ratios of some lakes in the Larsemann Hills in East Antarctica are determined to assess the lakes' chemical and isotopic evolution. The lakes occupied the natural depressions carved by glacial abrasions forming small basins, thus providing suitable water accumulation locales under lacustrine conditions. Lakes in the Grovness Peninsula, Stornes Peninsula, Brokenness Peninsula, Sigdoy and McLeod Islands were sampled. Weathering and reverse ion exchange reactions are found to regulate the ionic makeup of the lakes. The isotopic ratios were relatively enriched in the sampled lakes than the typical glacial meltwater fed lakes in other parts of the East Antarctica. Kinetic controlled ice-water fractionation, and evaporation processes are found to affect the isotopic evolution of the lake water in the Larsemann Hills region.

Keywords Ionic chemistry · Isotopic ratio · East Antarctic lakes · Larsemann Hills

1 Introduction

Antarctica, the remote continent, has been the fulcrum of climate studies in recent years. Oceanographers, geologists, geophysicists, marine biologists and climatologists are fascinated by the past climate records embedded in the ice cores, landforms and special features of the continent. Antarctica can be considered composed of two

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units, West Antarctica and East Antarctica, making up two-thirds of the landmass. A tiny fraction of this landmass is ice-free, which mainly consists of Nunataks. Among the ice-free regions, 1–2% contains coastal oases that have been exposed by the post-glacial retreat of the ice cap and isostatic rebound of the Earth's crust following the recent deglaciation (Hodgson 2012). Large oases are found in East Antarctica like the Vestfold Hills, Larsemann Hills, Bunger Hills, Schirmacher Oasis, Syowa Oasis etc. During the austral summer, meltwater accumulates in the land depressions, and lakes and ponds are formed in these oases. The Larsemann Hills, one of the significant oases in East Antarctica, sustains many lakes varying in depth, quality, water spread area, and water availability (seasonal or perennial). As these lakes are fed by glacial meltwater, the chemical composition depends mainly on the precipitation and regional bedrock geology. However, continuous cycles of freezing, thawing and evaporation alter the primary composition giving distinct chemical signatures. Similar to the chemical composition, stable isotope ratios are also varied in these lakes. Earlier studies have focussed on many aspects of lakes in the Larsemann Hills (Gasperon et al. 2002; Kaup and Burgess 2002; Hodgson 2012; Wand et al. 2011; Verleyen et al. 2012; Bharti and Niyogi 2015; Nakai et al. 1975; Horita 2008; Quayle 2002; Gasperon 2002; Beg and Asthana 2002; Verleyen 2004; Sabbe et al. 2004; Shrivastava et al. 2012). This study presents the ionic and isotopic characterization of selected lakes in the Larsemann Hills of East Antarctica.

2 Materials and Methods

The Larsemann Hills is the ice-free coastal oasis in the Ingrid Christensen Coast of Princess Elizabeth Land in East Antarctica (69°30'S, 76°19'58" E). It is spread in approximately 50 km² and includes about 150 lakes with different ionic character. Stornes and Broknes are the two significant peninsulas in the Larsemann Hills. There are other minor peninsulas and many coastal islands in the area. The Indian research station 'Bharti' is located in the central part of the Larsemann Hills, which is about ~12 km² in the area.

The introductory geology of the Larsemann Hills consists of supracrustal volcanogenic and sedimentary rocks metamorphosed under granulite facies conditions. The supracrustal rocks are intruded by several generations of pegmatites and granites and are underlain by and possibly derived from the proterozoic orthopyroxene-bearing orthogneiss basement (ATCM 2014). Lakes are formed in the land depressions caused by glacial erosion.

We sampled water to form 16 lakes from the Broknes Peninsula (BP), Stornes Peninsula (SP), Grovnes Peninsula (GP, near Bharti Promontory), Sigdoy Island (SI) and McLeod Island (MI) in the Larsemann Hills during the 29th Indian Antarctic Scientific Expedition. The study area's location map is provided in Fig. 1, and a few photographs of water sampling are given in Plate 1. Samples were collected in pre-cleaned plastic bottles, and physicochemical parameters were determined in situ, and standard procedures were followed to find out the ionic composition (APHA

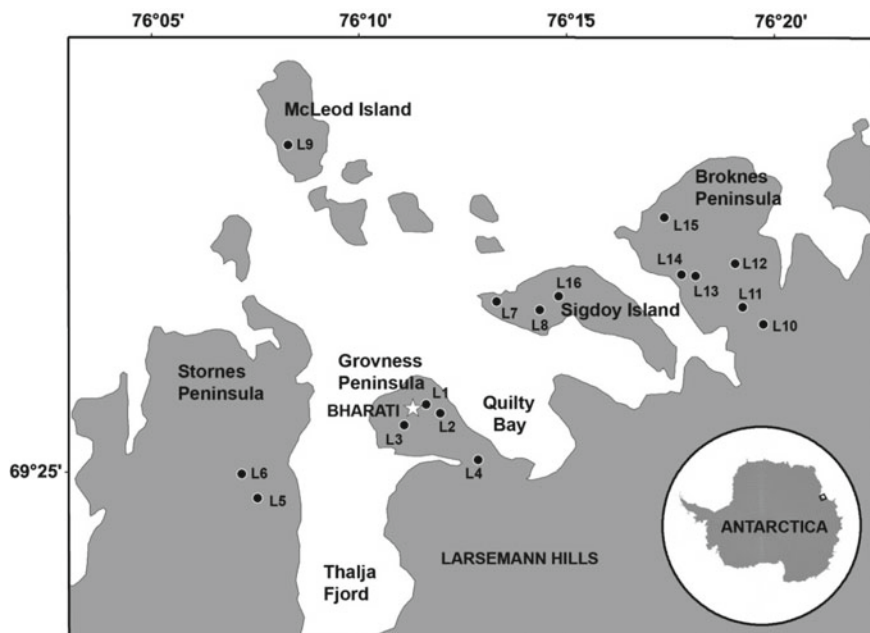


Fig. 1 Sampling locations of the lakes in Larsemann Hills, East Antarctica



Plate 1 Water sampling from the lakes

1995). For isotopic measurements, water samples were collected in High-density polyethylene (HDPE) bottles, and the ratios were determined in an off-axis integrated cavity output spectroscopy system (IWA-45EP, Los Gato's research), with an external precision of $\pm 0.1\%$ for $\delta^{18}\text{O}$ and $\pm 0.5\%$ for δD . The results were expressed in δ as,

$$\delta = \left[\frac{R \text{ sample}}{R \text{ standard}} - 1 \right] \times 1000$$

Table 1 Location details of the sampled lakes in Larsemann Hills, East Antarctica

Sl. no	Code	Location name	Type
1	L1	Grovness Peninsula	Surface shallow depression storage
2	L2	Grovness Peninsula	Surface shallow depression storage
3	L3	Grovness Peninsula	Surface shallow depression storage
4	L4	Grovness Peninsula	Surface shallow depression storage
5	L5	Stornes Peninsula	Precipitation dominant
6	L6	Stornes Peninsula	Precipitation dominant
7	L7	Sigdoy Island	Surface shallow depression storage
8	L8	Sigdoy Island	Surface shallow depression storage
9	L9	McLeod Island	Precipitation dominant
10	L10	Broknes Peninsula	Surface shallow depression storage
11	L11	Broknes Peninsula	Precipitation dominant
12	L12	Broknes Peninsula	Precipitation dominant
13	L13	Broknes Peninsula	Precipitation dominant
14	L14	Broknes Peninsula	Precipitation dominant
15	L15	Broknes Peninsula	Precipitation dominant
16	L16	Sigdoy Island	Surface shallow depression storage

Where R represents either $^{18}\text{O}/^{16}\text{O}$ or D/H ratio.

Details of the lakes selected for the study are provided in Table 1. For isotopic measurements, water was collected from all the 16 lakes, whereas 13 lakes were chosen for ionic determination. All the lakes were shallow and contained freshwater.

3 Results and Discussion

3.1 Hydrochemical Composition of the Lakes

Table 2 illustrates the hydrochemical data of the lakes in the study area. pH varied from slightly acidic (6.2) to alkaline (7.7) in the lake water. $\text{pH} > 7$ was noted in the Sigdoy and McLeod island lakes compared to the peninsular lakes (Grovness, Broknes and Stornes). Electrical conductivity (EC) showed large variation with a minimum of $13.8 \mu\text{S}/\text{cm}$ at L6 (Stornes Peninsula) to the maximum of $1330 \mu\text{S}/\text{cm}$ at L9, McLeod Island. Based on EC, the lakes can be categorized into three, such as $\text{EC} < 500 \mu\text{S}/\text{cm}$ (L1–L7, L12–L13) and $\text{EC} = 500\text{--}1000 \mu\text{S}/\text{cm}$ (L11) and $\text{EC} > 1000 \mu\text{S}/\text{cm}$ (L8–L10). Lakes in the GP and SP belonged solely to the first category, whereas the lakes in the MI and one each from SI and BP belonged to the higher EC category. Only one lake in BP was in the second category. The lakes in the BP showed a large variation in ionic content falling in the three categories. Similarly,

Table 2 Hydrochemical composition of the selected lake water in the study area

Code	pH	EC ($\mu\text{S}/\text{cm}$)	TDS (ppm)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Cl (mg/L)	HCO ₃ (mg/L)	SO ₄ (mg/L)
L1	6.38	360	192	3.4	5.1	48.5	2.1	80.2	12.9	9.7
L2	6.99	383	203	5.0	3.1	53.5	2.9	84.0	13.1	19.3
L3	6.86	205	112	1.7	4.1	29.4	1.9	47.7	10.6	14.5
L4	7.27	234	127	6.7	5.1	29.9	1.8	51.5	9.8	29.0
L5	6.29	274	145	5.0	3.1	32.4	1.9	57.3	6.7	9.7
L6	6.22	13.8	7	1.7	0.0	1.5	1.2	1.9	4.0	4.8
L7	6.4	141	72	3.4	1.0	17	1.5	22.9	3.3	14.5
L8	7.66	1210	610	25.2	23.5	130	7.3	274.8	3.9	120.8
L9	7.27	1330	690	10.1	21.5	170	8.7	324.5	35.9	33.8
L10	7.06	1210	650	15.1	21.5	140	6.6	284.4	39.9	38.6
L11	6.41	532	284	3.4	5.1	75	3.8	110.7	19.0	24.2
L12	6.75	373	195	6.7	5.1	43.5	2.3	61.1	33.0	24.2
L13	6.65	163	87	3.4	2.0	21.2	1.6	26.7	7.3	4.8

the SI lakes belonged to one of the lowest and highest ionic content categories simultaneously. Overall, the islands' lakes showed higher conductivity, perhaps due to the sea's proximity or increased evaporation as being closed basins. Among the major ions, calcium and chloride ions dominated invariably in all the sampled lake water. In the cationic part, either K or Na was present next to Ca; and among the anions, sulphate was present substantially than bicarbonate ions in most lakes.

3.2 Major Hydrochemical Interactions

The lake water's inter-ionic relations were determined with Pearson's product momentum correlation (Table 3). Most of the ions in the study area's lakes were correlated with each other either strongly or moderately. Bicarbonate ion was the only ion that did not show any relationship with any other except for Ca. The strong correlation among the ions of the lakes can be attributed to their common origin.

To find out the origin of ions in the lake water, Gibb's classification was used (Fig. 2), which can differentiate between the three significant sources such as (1) evaporation/seawater dominant, (2) rock-water interaction/weathering dominant and (3) precipitation prevalent.

Though the concentration of ions in these lakes was low, except for one lake in the Stornes Peninsula (SP), all other lakes showed the predominance of weathering reactions. As these lakes are shallow and primarily temporary, the host rocks' interactions are significant. As obtained in Piper's diagram, the major geochemical facies present in the lake water were Ca-Cl, pointing to lake water's strong interaction with the host rocks. It can be considered that in the pristine waters of Antarctica, mineralogy defines the ionic character of the lakes (Fig. 3).

Table 3 Correlation coefficients of the hydrochemical components of lakes in the Larsemann Hills (*Significant coefficients are given in bold and italics*)

	pH	EC	TDS	Na	K	Ca	Mg	Cl	HCO ₃	SO ₄
pH	1									
EC	0.69	1								
TDS	0.68	1.00	1							
Na	0.77	0.81	0.80	1						
K	0.75	0.98	0.98	0.88	1					
Ca	0.66	0.99	0.99	0.74	0.95	1				
Mg	0.69	0.99	0.98	0.78	0.96	0.99	1			
Cl	0.69	1.00	1.00	0.79	0.98	0.99	0.99	1		
HCO ₃	0.27	0.61	0.63	0.22	0.53	0.65	0.57	0.60	1	
SO ₄	0.77	0.70	0.68	0.94	0.77	0.63	0.68	0.67	0.03	1

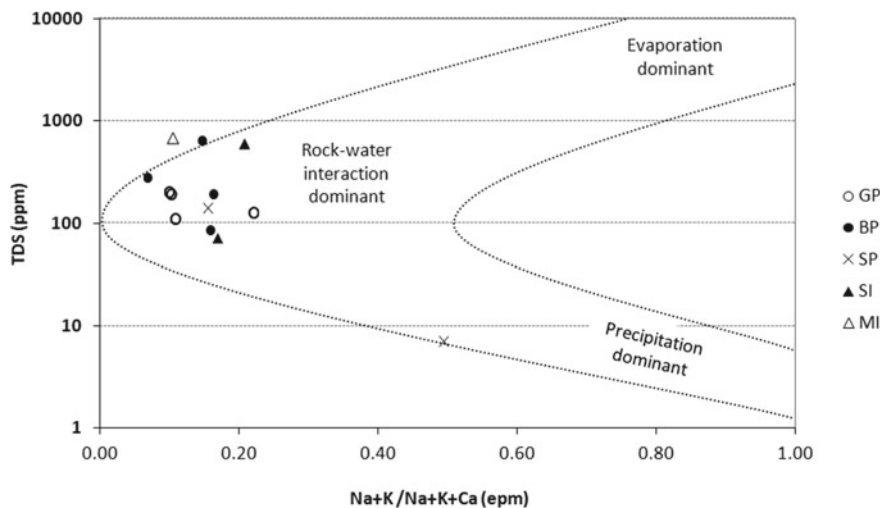


Fig. 2 Gibb's classification of lake water in the Larsemann Hills

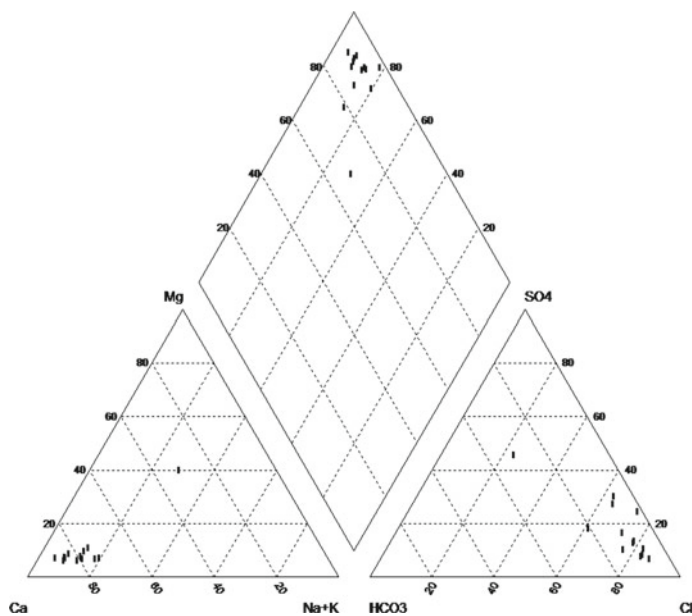


Fig. 3 Piper diagram of lake water of the Larsemann Hills, East Antarctica

Different ionic relations were plotted to understand the significant weathering reactions responsible for the lake water's ionic composition (Fig. 4a–f).

The relation of the lakes' total alkalinity, which is mainly due to the bicarbonate alkalinity, with total cations (TZ⁺) (Fig. 4a) showed an excess of cations, which cannot be balanced by the bicarbonate ion alone. It has been reported earlier that the rate of weathering reactions is very high in Larsemann Hills's peninsulas (Kiernen et al. 2009). Consequently, the dissolved carbon dioxide was used up, and accordingly, bicarbonate ion concentration is lesser in these lakes. Ca and Mg ions were plotted with bicarbonate and sulphate ions (Fig. 4b), and as can be seen, there is an excess of Ca and Mg, which points to additional sources of these ions. Since the geology of the area is determined mainly by silicate rocks, silicate weathering can be the lake's ions source. To find out the silicate weathering, Na + K and Ca + Mg were plotted against total cations separately (Figs. 4c, d). Na and K were not varying linearly with total cations or did not fall on the 0.5TZ⁺ line, and there can be a possibility of Ca/Na exchange reactions. However, as the Ca and Mg ions were

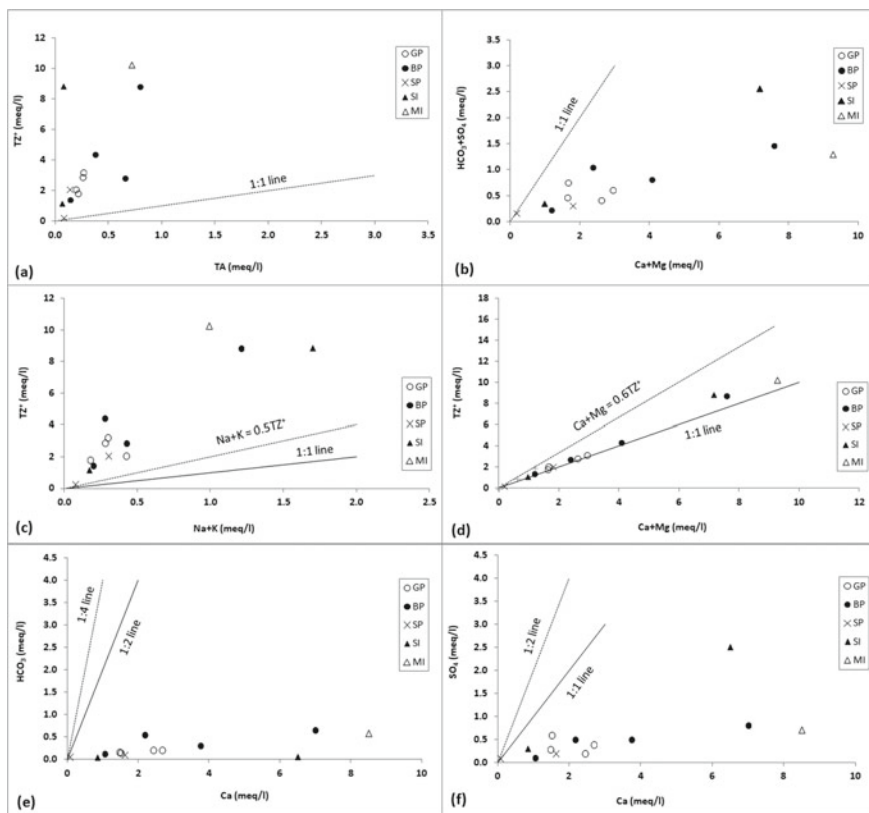


Fig. 4 Variation of **a** Total alkalinity with total cations **b** Calcium and Magnesium with Bicarbonate and Sulphate **c** Sodium and Potassium with total cations **d** Calcium and Magnesium with total cations **e** Calcium with Bicarbonate **f** Calcium with Sulphate

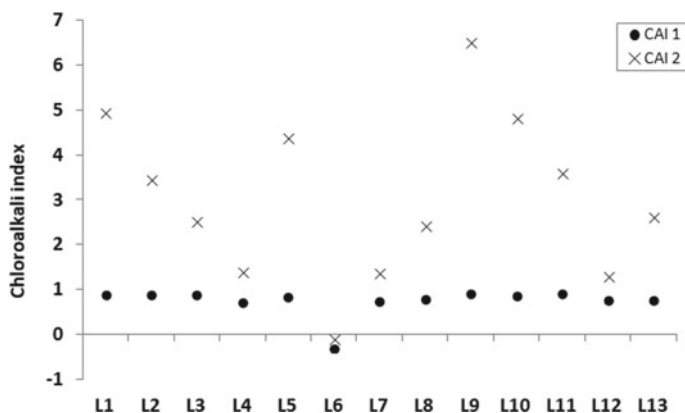


Fig. 5 Chloro alkali indices in the lake water of Larsemann Hills

varying linearly with total cations in most of the lakes, these ions may have originated by silicate weathering reactions. Ca to Mg molar ratios were >2 in most of the lakes, indicating the predominance of silicate weathering reactions (Katz et al. 1998). Moreover, the plot of Ca with bicarbonate and sulphate (Figs. 4e, f) showed excess calcium in the lake water due to different geochemical processes such as exchange reactions contributing these ions.

Chloroalkali indices (CAI 1 & 2) devised by Schoeller (1965, 1967) were used to determine the lakes' ion exchange reactions. If both the indices are negative, there is an exchange of Ca and Mg of the water with Na and K of the earth material. If reverse ion-exchange reactions are occurring, the indices will be positive and accordingly, Ca and Mg of the rock material will get exchanged with Na and K ions in water.

Except for L6 of SP, all the lakes showed reverse ion-exchange reactions, contributing Ca and Mg to the lake water (Fig. 5). Hence apart from silicate weathering, Ca ions are added to the water by the reverse ion exchange process accounting for the excess Ca present in the water. A direct ion-exchange reaction was observed in L6, in Stornes Peninsula, and the primary source of Na and Ca into this lake water is the weathering of silicate minerals.

Table 4 shows the principal component analysis results of the lake water in the study area. Two major factors were extracted with varimax rotation, which could explain 93.7% of the total variance of data. Eigen values >7 were selected in this analysis. In factor 1, pH, SO_4 , Na, and K showed strong loadings, and EC, TDS, Mg and Cl showed moderate loading. This factor could alone explain 80.7% of the total variance. EC, TDS, Ca, Mg, Cl and HCO_3 loaded strongly and K moderately in Factor 2.

From the PCA, two dominant origins of ions can be discerned: seawater and, second, weathering reactions. The entrapped seawater in the closed basins or the marine aerosols transported by the solid Katabolic winds may be responsible for the lakes' ionic composition. As seen in the previous sections, weathering and exchange

Table 4 Varimax rotated factor loadings of PCA analysis of lake water of Larsemann Hills

	Factor 1	Factor 2
pH	0.804	0.283
EC	<i>0.637</i>	0.765
TDS	<i>0.616</i>	0.782
Na	0.918	0.303
K	0.725	<i>0.673</i>
Ca	0.563	0.814
Mg	<i>0.630</i>	0.751
Cl	<i>0.624</i>	0.770
HCO ₃	-0.106	0.926
SO ₄	0.970	0.105
Eigenvalue	8.068	1.301
% total variance	80.7	13.0
Cumul. %	80.7	93.7

reactions form the second component. As the lakes are shallow and fleeting, evaporation can be another process that increases the ionic concentration in lake water. Since Lake L6 showed clear precipitation origin, to check the evaporation effect, this lake was omitted. Since the Na/Cl molar ratio remains constant even when EC is increased due to evaporation, these two variables' covariance was checked (Fig. 6).

In Fig. 6, the dotted line gives the linearity of lakes without L6 and the solid line with L6. If L6 is considered an outlier, the line's slope is very close to 0, i.e. evaporation is a dominant process in these lake systems. To get a clear picture of these

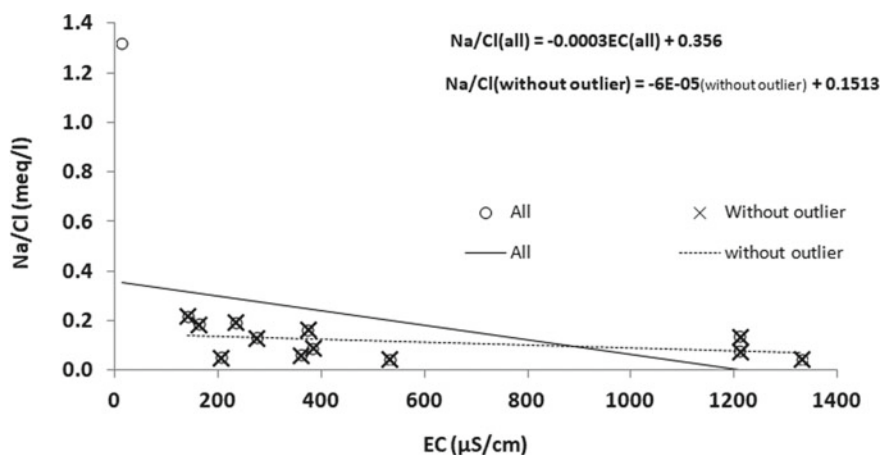


Fig. 6 Variation of EC with Na/Cl molar ratio in the lake water of Larsemann Hills

processes, isotopic ratios were determined, the observations of which are provided in the subsequent sections.

3.3 Isotopic Characterization of Lakes of Larsemann Hills

The stable isotope composition of 16 lake samples of the study area was determined, and the results are depicted in Table 5. Similar to the chemical composition, a considerable variation is observed in these lake waters' isotopic ratios. $\delta^{18}\text{O}$ ranged between -7.6‰ and -17.9‰ and δD between -108.7‰ and -146.5‰ .

Compared to other lakes, such as in the Schirmacher Oases in East Antarctica ($\delta^{18}\text{O} = -30\text{‰}$, Gopinath et al. 2020), Larsemann Hills's lakes have an enriched isotopic composition. L9, located in the McLeod island, was the most enriched ($\delta^{18}\text{O} = -7.6\text{‰}$). The lakes in the Groveness Peninsula (GP) has an average isotopic composition of ($\delta^{18}\text{O} = -14.6\text{‰}$, $\delta\text{D} = -121.3\text{‰}$); lakes in Stornes Peninsula (SP) has $\delta^{18}\text{O} = -16.8\text{‰}$, $\delta\text{D} = -141.7\text{‰}$, Sigdoy Island (SI) has $\delta^{18}\text{O} = -12.5\text{‰}$, $\delta\text{D} = -110.6\text{‰}$ and the Broknes Peninsula (BP) has $\delta^{18}\text{O} = -14.3\text{‰}$, $\delta\text{D} = -121.9\text{‰}$. Lakes located in the islands were enriched, and, on average, a difference of 5‰ was noted as that of the peninsular lakes. We separated the lakes into precipitation dominant and surface depression storage and compared the isotopic composition (Fig. 7).

Table 5 Stable isotope data of lake waters of Larsemann Hills, East Antarctica

Sl. no	Code	Location name	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	d-excess
1	L1	GP	-17.4	-138.7	0.08
2	L2	GP	-12.7	-110.6	-9.08
3	L3	GP	-13.4	-113.3	-6.02
4	L4	GP	-14.8	-122.4	-4.09
5	L5	SP	-17.9	-146.5	-3.12
6	L6	SP	-16.8	-141.7	-7.06
7	L7	SI	-15.0	-130.2	-10.4
8	L8	SI	-11.8	-111.0	-16.3
9	L9	MI	-7.60	-108.7	-48.3
10	L10	BP	-12.7	-112.0	-10.5
11	L11	BP	-12.8	-117.0	-14.6
12	L12	BP	-11.0	-104.7	-16.6
13	L13	BP	-17.3	-138.7	-0.66
14	L14	BP	-17.9	-142.5	0.98
15	L15	BP	-14.0	-116.5	-4.19
16	L16	SI	-13.3	-110.3	-4.31

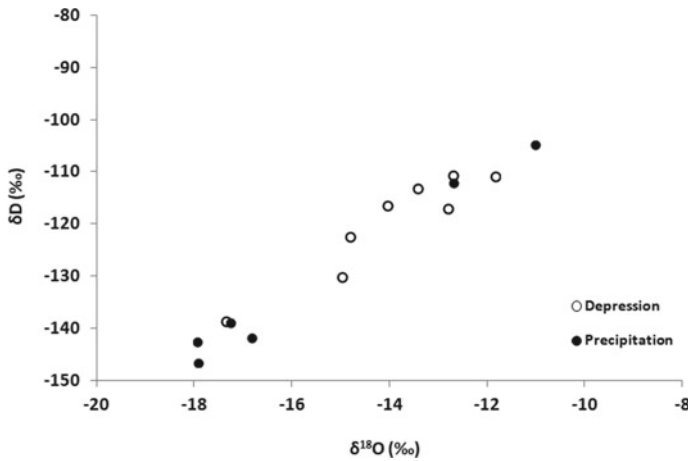


Fig. 7 Isotopic composition of the precipitation dominant lakes and shallow surface depression lakes in Larsemann Hills, East Antarctica

As expected, most of the lakes in the precipitation-dominant category were depleted in heavier isotopes than the shallow depression storage lakes. However, Lake L1 (GP), though being depression storage, was depleted in heavier isotopes may be because of the inflow of isotopically depleted melt eater. Similarly, L9 (MI) and L12 (BP) had isotopic enrichment though they were precipitation dominant. The contrasting behaviour can be attributed to the evaporation processes occurring in the lakes.

3.4 $\delta^{18}\text{O}$ - δD Covariance in the Lake Water

Figure 8 shows the covariation of $\delta^{18}\text{O}$ and δD in the lake waters. The lake water line (LWL) has a slope of 4.54, close to that observed for systems dominant in evaporation. Horita (2009) have shown that in a naturally freezing method, the remaining water will be depleted in heavier isotopes and will have a slope of 5–6 in the regression plot of $\delta^{18}\text{O}$ - δD that are similar to the slopes due to evaporation processes.

The lake water line's intersection point (LWL) with the global meteoric water line represents the isotopic composition of the region's precipitation. Thus $\delta^{18}\text{O} = -20\text{‰}$ and $\delta\text{D} = -144\text{‰}$ can be considered as the initial isotopic composition of precipitation. A few lakes in the BP and SP have δ values close to this value but are more enriched, probably due to the kinetically controlled ice-water fractionation processes. However, the slope of LWL is mainly defined by other lakes in which evaporation can be the dominant process. The d-excess values obtained also are in accordance. The evaporation process enriches the water body lowering the d-excess

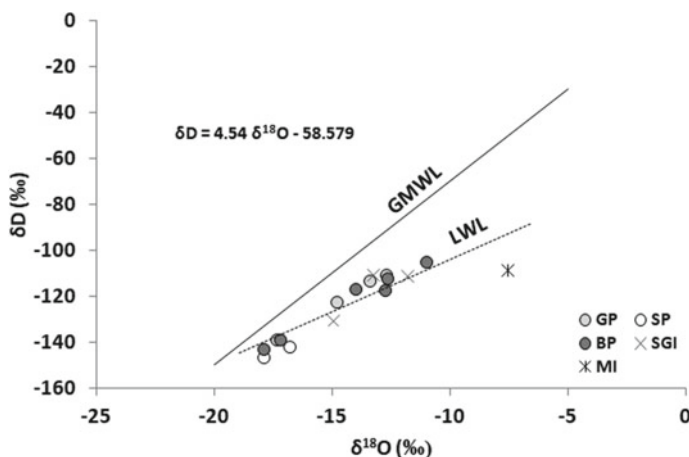


Fig. 8 Regression plot $\delta^{18}O$ versus δD of the lake waters. The evaporation line or lake water line is also given

of the residual water. The island lakes have the lowest d-excess values being shallow basins with entrapped seawater.

4 Conclusions

Hydrochemical and isotopic characteristics of the lakes in the Larsemann Hills in East Antarctica were determined. Lakes in the Grovness Peninsula, Stornes Peninsula, Broknes Peninsula, Sigdoy and McLeod Islands were selected for the study. The island lakes' pH was slightly alkaline, and the major hydrochemical facies identified in the lake water was Ca–Cl. There was strong interaction of lake water with the host rocks, and weathering and reverse ion exchange processes were the source of ions. The lakes have an enriched isotopic composition than the lakes in the Schirmacher Oases. The isotopic ratios could identify the lakes as precipitation dominant and evaporation dominant. The kinetic controlled ice-water fractionation and evaporation processes control the lake water's isotopic composition in the Larsemann Hills.

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