



Isotope hydrochemistry of the lakes in Schirmacher Oasis, East Antarctica

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The study aims to find out the ionic and isotopic compositions of some lakes in the Schirmacher Oasis in east Antarctica. The water samples were collected from 12 lakes near the Indian Antarctic station, Maitri. The chemistry of lake water indicates contribution from glacial melt water and lithology of the area. Evaporation from shallow lakes was also found to be controlling the lake water chemistry. The isotopic concentration of the lake waters also indicated input from the melt water from adjacent glaciers. δD varied between -167.2 ‰ and -250.2 ‰ and $\delta^{18}O$ from -18.0 ‰ to -31.2 ‰. It was found that diffusion controlled kinetic effect at the liquid-ice interface for different water isotopologues and evaporative enrichment of heavier isotopes from open water bodies determined the slope of the regression line of the lake water.

[**Keywords:** Ionic composition, Polar lakes, Schirmacher Oases, Stable isotopes]

Introduction

The Polar regions, especially Antarctica which contains 90 % of the world's total ice (70 % of the freshwater ice) has a decisive part in global climatic change¹⁻³. According to Hodgson⁴, only 0.32 % of the Antarctic continent is ice-free and mainly consists of mountain peaks (nunataks) protruding from the polar ice cap. Due to the postglacial retreat of the ice cap and isostatic rebound of the Earth's crust following the most recent deglaciation, 1–2 % of the ice free region has been exposed which includes the coastal oases. The McMurdo Dry Valleys are the largest oasis near the Ross Sea and others are situated in eastern Antarctica which include the Vestfold Hills, Larsemann Hills, Bunger Hills, Schirmacher Oasis, Syowa Oasis, and on the Antarctic Peninsula at Ablation Point on the east coast of Alexander Island⁴. Though the Antarctica continent contains more than 70 % of global freshwater, the availability of liquid freshwater is least there compared to other continents. However, water bodies containing liquid water for at least part of the year is a common feature. This is because water accumulates in areas where solar radiation and advection heat promote melting of ice. Due to this process bare ground is exposed, its albedo drops and more radiation is absorbed and further

increases melting. Hence, water in liquid form is found on ice-free ground. Beneath the glaciers and ice sheet also liquid water occurs. Lakes and ponds are formed in places where the water in glaciers and ice sheets is accumulated⁴. Kaup⁵ observed that in Schirmacher, the radiation processes of the lakes is decided by many factors mainly by the differences in the albedo of new and old ice, the amount of suspended matter and secondarily by the differences in areas covered by snow. According to Hodgson⁴, the increase of radiation in water is mainly determined by the irregularities at the lower surface of the ice. Accordingly, the radiation regime determines seasonal variations in water temperature. The cooling and warming effects are determined by the glaciers and rocks respectively. Cooling of the lake water by the inflowing melt water has the same effect as the turbulent heat exchange with atmosphere in summer. Thus the variation in snow and ice cover changes all ecological variables and make the polar lakes the early detectors of environmental change⁶.

The chemical concentration and composition of non-marine waters in Antarctica show considerable variation, indicating different source of solutes⁷. They can be derived from the glacial melt water and become concentrated as a result of freezing or evaporation. The

salt content of lakes in the coastal environment is generally derived from the sea; either the result of sea water trapped by isostatic uplift or due to aeolian transport of aerosol and sea spray⁸. In addition to this, interaction with the rocks and ground water flow can also contribute to the solute regime. Hence, the cumulative effect of physical processes such as freezing, evaporation, sublimation, and mixing of water from different reservoirs determine the stable isotopic and chemical makeup of precipitation, resulting in redistribution of isotopes and dissolved solids. The lakes in East Antarctic region has been a subject of study in many aspects like biology, sedimentology, hydrogeochemistry, hydrology, limnology etc.⁹⁻¹⁴.

The stable isotope ratios of water ($\delta^{18}\text{O}$ and δD) do not change unless by mixing of water from a different reservoir or by processes like evaporation and sublimation. The water bodies of Antarctica have been investigated for stable isotopes by many investigators¹⁵⁻¹⁹. They highlighted the vital role played by the Antarctica lakes in the water balance of the Schirmacher Oasis, especially in the estimation of contribution of the melt water from the glaciers and the snow/ice fields of the oasis through stable isotopic composition. In a study by Haberlandt *et al.*¹⁵, all water bodies of the Central Queen Maud Land are found to be of freshwater type. The salt content was relatively high (up to about 500 mg/L) compared with that of the regional snow and ice which feed the lakes. They related the local differences in salt concentration and chemical type of water to the evaporation of drain less lakes and geochemical peculiarities of the different catchment areas. The isotope data of the large drained lakes of the Schirmacher Oasis were within the range of values for Holocene precipitations accumulated in the glacial surroundings ($\delta^2\text{H}_{\text{SMOW}} = -210$ to -240 ‰, $\delta^{18}\text{O}_{\text{SMOW}} =$ around -30 ‰) whereas some lakes were predominantly fed by the Pleistocene basal layer of the regional ice cover.

In this study, the lakes near the early Indian Station in Antarctica, Maitri, and in the Schirmacher Oasis are explored for the hydrochemical and stable isotopic investigation.

Materials and Methods

The Schirmacher Oasis ($70^{\circ}44'30''$ S to $70^{\circ}46'30''$ and $11^{\circ}22'40''$ E to $11^{\circ}54'00''$ E) is a narrow strip of ice free region covering an area of about 35 km^2 laying in the east-west direction (Fig. 1). The central part of the Oasis has maximum width of about 2.7 km

and has undulating topography with small hills ($\sim 200 \text{ m}$ elevation) and depressions formed by glacial valleys and lakes. The region is characterized by deglaciated landscape interspersed with more than 100 freshwater lakes²⁰. The lakes can be classified as proglacial, landlocked or inland and epiglacial lakes that occur in well defined lineament and glacial basins formed during late Pleistocene-Holocene period.

The Schirmacher Oasis region is geomorphologically distinguishable into three units: i) polar ice sheet, ii) Schirmacher mainland including lakes, and iii) coastal-shelf area. All the three units extend in east-west directions paralleling the coastline (Fig. 1). The polar ice sheet, which contains abundant sand and silt-size sediments, covers a large area in the south. The exposed mainland unit mostly represented by high-grade metamorphic rocks²¹, shows an undulating topography with low altitude hills of 50 to 200 m elevation and inland lakes formed due to glacier erosion. Various sub-glacial tills, glacial valleys, and polished bedrock are easily recognizable in this unit. The third unit represented by the coastal-shelf region is marked by the presence of coastal sand, which is largely mixed with sediments from inland and the polar ice sheet, transported through melt water channels¹⁰.

Lake water samples were collected during the 29th Indian Antarctic Scientific Expedition (2009-2010). Samples were collected from 12 locations including the Priyadarshini Lake and the shallow ponds from Schirmacher Oasis during austral summer (17th February – 24th February). Priyadarshini Lake is one of the largest landlocked lakes with about 0.75 km^2 water spread area. pH and electrical conductivity (EC) were measured *in situ*, and the major cation and anion concentrations were determined in the laboratory, following standard analytical procedures²². Triplicate analyses of each sample were done to check the analytical reproducibility and the results are the

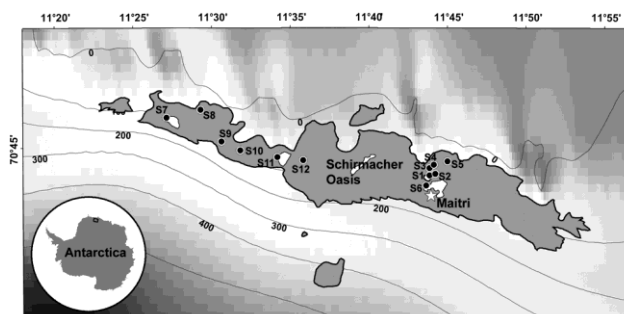


Fig. 1 — Lake water Sampling locations at Schirmacher Oasis

average of these. High density polyethylene (HDPE) bottles were used for collection of lake water for isotopic determination and stable isotopes were measured using the off axis integrated cavity output spectroscopy (IWA-45EP, Los Gatos research), with an external precision of ± 0.1 ‰ for $\delta^{18}\text{O}$ and ± 0.5 ‰ for δD . The results were expressed in δ as,

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

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

Results

The lake water samples showed pH in the range 5.9 to 7.3 with an average of 6.6. The slightly acidic nature of lake water in the Schirmacher Oasis has been reported earlier by Ali *et al.*²³. Electrical conductivity (EC) showed large variation among the samples. Highest value of 511 $\mu\text{S}/\text{cm}$ was noted at M5. In fact, only three lakes (M3, M5 & M12) recorded EC > 200 $\mu\text{S}/\text{cm}$ and in the rest of samples, EC was below 100 $\mu\text{S}/\text{cm}$. Electrical conductivity values shows that the lakes are fresh water in character.

The ionic concentration of the lake water samples was low (Table 1). In majority of the samples, Ca and Na dominated over other cations and SO_4 was the predominant anion. In some samples, chloride was below detection limit. Earlier studies have shown that the lakes in Schirmacher Oasis are with minimal marine influence due to the distance from the sea and those which were close to the ice sheet were characterized by a higher Ca to Na ratio²⁴. δD varied from -167.2 ‰ to -250.2 ‰ and $\delta^{18}\text{O}$ from -18.0 ‰ to -31.2 ‰ in the sampled lakes of the region.

Discussion

The ionic composition of Antarctic lakes are determined by lake-ice thawing which can either result in more diluted lake water due to the addition of melt water of ionic content or, more concentrated lake water if marine aerosols are accumulated in the snow and ice. In the case of Schirmacher Oasis, all lakes are in elevations above the Holocene marine limit that had no hydrological contact with the ocean in the past⁴ and has glacial origin, in contrast to the saline lakes and ponds in East Antarctica. The lakes in East Antarctica are isolation basins of low elevations. Many of the lakes in Schirmacher Oasis are of Holocene age and are thus relatively young²⁵. The lakes are flushed by continuous supply of melt water in the summer by the streams from the East Antarctic Ice Sheet or from permanent snow banks upstream. The observed higher Ca/Na ratio of the lake water also affirmed the source from the continuous flushing with glacial melt water. The association of dissolved ions in the lakes was identified with correlation coefficients (Table 2). Since all the major cations and anions are found to be significantly correlated with one another ($\alpha = 95\%$), the ions can be assumed to have originated from a single prominent source. It may be noted that the correlation between sulphate and bicarbonate ions was less significant probably due to the possible source of sulphate from bacterially produced DMS. The relatively excess concentration of sulphate compared to chloride can be due to the oxidative dissolution of dimethyl sulphide produced by the marine microorganism in the Antarctica aerosols.

In most of the lake water samples, either Ca or Mg were the dominant cations and bicarbonate and

Table 1 — Chemical composition of lake waters of Schirmacher Oasis

Code	pH	EC ($\mu\text{S}/\text{cm}$)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Cl (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)
S 1	6.4	15.7	0.8	0.5	1.3	1.3	3.8	4.8	2.5
S 2	7.1	9.0	1.7	0.0	1.4	1.3	3.8	1.9	10.1
S 3	7.2	105	6.7	3.1	8.4	2.4	11.5	29.0	24.5
S 4	6.3	18.9	1.7	1.0	1.5	1.3	3.8	4.8	1.8
S 5	7.1	511	20.2	15.3	38.4	11.5	53.4	67.6	54.8
S 6	6.6	14.2	1.7	0.0	1.2	1.3	5.7	2.1	2.2
S 7	6.4	14.4	1.7	1.0	1.1	1.3	1.9	9.7	2.1
S 8	5.9	76.6	1.7	1.0	8.7	1.4	15.3	4.8	2.3
S 9	6.2	8.2	1.7	0.0	1.0	1.3	B.D.L.	2.4	4.3
S 10	6.1	8.2	1.7	0.0	1.0	1.3	B.D.L.	4.8	2.1
S 11	6.8	4.1	1.7	0.0	0.9	1.2	B.D.L.	4.8	2.3
S 12	7.3	218	13.5	7.2	16	5.3	22.9	77.3	5.7
Mean	6.6	84	4.6	2.4	6.7	2.6	10.2	17.8	9.6
Max	7.3	511	20.2	15.3	38.4	11.5	53.4	77.3	54.8
Min	5.9	4.1	0.8	0.0	0.9	1.2	B.D.L.	1.9	1.8

B.D.L. – Below Detection Limit

Table 2 — Correlation matrix of dissolved ions in the lake water of Schirmacher Oasis

(Note: Significant correlations are given in bold)

	pH	EC	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄
pH	1								
EC	0.50	1							
Ca	0.47	1.00	1						
Mg	0.51	0.99	0.98	1					
Na	0.63	0.97	0.96	0.97	1				
K	0.53	0.99	0.98	0.99	0.98	1			
Cl	0.46	0.99	0.99	0.97	0.94	0.97	1		
HCO ₃	0.53	0.89	0.88	0.88	0.83	0.87	0.86	1	
SO ₄	0.67	0.86	0.84	0.85	0.95	0.89	0.82	0.64	1

sulphate were present in higher concentration than chloride. The sources of these ions can be the weathering reactions of the rock materials bearing carbonates and silicates. In the Ca+Mg vs HCO₃+SO₄ plot (Fig. 2a), the samples falling on the 1:1 equiline suggested that these ions are derived from the carbonate and sulphate minerals²⁶. If silicate weathering is the only source of calcium and magnesium ions, bicarbonate ion alone can balance these.

Moreover, in silicate terrains, if calcite weathering is the origin of calcium and bicarbonate ions, the equivalent ratio of dissolved Ca²⁺ and HCO₃⁻ is 1:2 and the ratio is 1:4 if it is from dolomite weathering²⁷. Likewise, the Ca²⁺/SO₄²⁻ ratio is 1:1, if the calcium and sulphate are originated by the dissolution of gypsum or anhydrite²⁸. In the plot of Ca vs bicarbonate (Fig. 2b), some samples were following the 1:2 line indicating calcite weathering and some has excess of Ca compared to bicarbonate. In the case of Ca vs SO₄²⁻ plot (Fig. 2c), some were plotting along the 1:1 and 1:2 lines and there are excess of both Ca and SO₄ ions. Samples falling on the 1:1 line denoted gypsum and anhydrite dissolution, whereas excess Ca points for additional source.

The Ca to Mg molar ratio of the lake water samples was mostly below 1, and in a few, it was greater than 2.0. According to Mayo and Loukas²⁹, if the molar ratio of these two ions is equal to one, dissolution of dolomite will occur, whereas a higher ratio indicates calcite dissolution. The molar ratio of the lake water samples in the Schirmacher Oasis is mostly less than one, indicating dissolution of dolomite. Further Katz *et al.*³⁰, has shown that higher Ca/Mg molar ratio (> 2), is indicative of dissolution of silicate minerals. In a few samples, the ratio was > 2, indicating silicate weathering can be a source of these ions in the lake water. To find out this source of ions, covariance of ions were examined (Fig. 3a) with the ratio between Na+K and total cations (TZ⁺). In the plot, samples

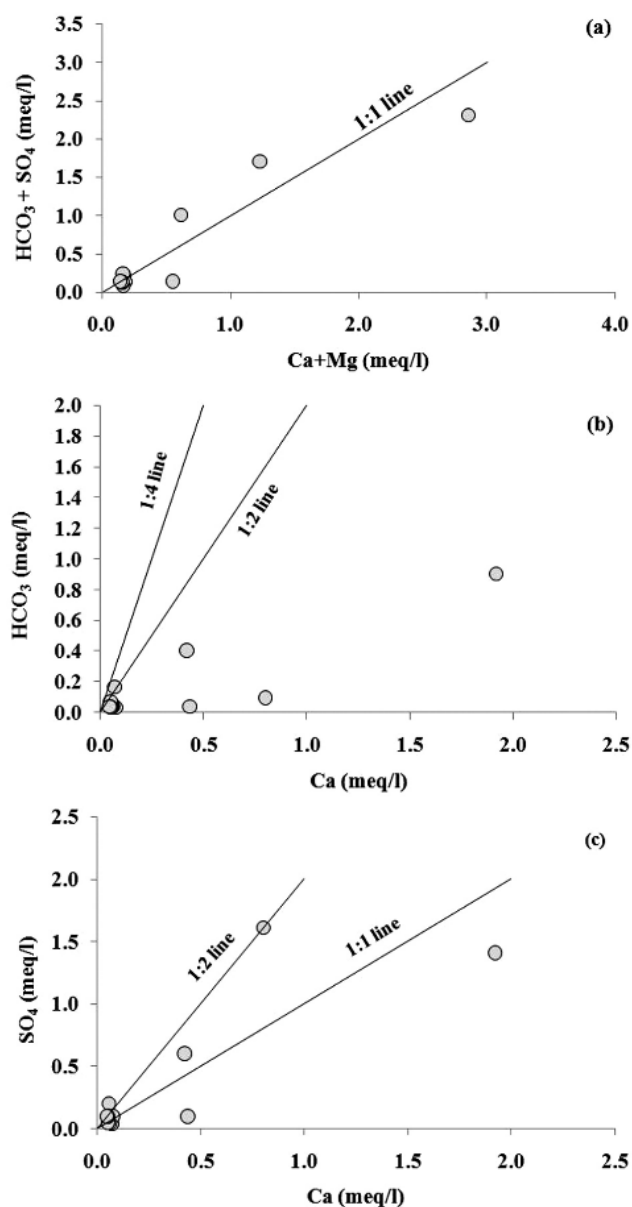


Fig. 2 — Covariance of: a) Ca and Mg with HCO₃ and SO₄, b) Ca with HCO₃, and c) Ca with SO₄; of lake water of Schirmacher Oasis

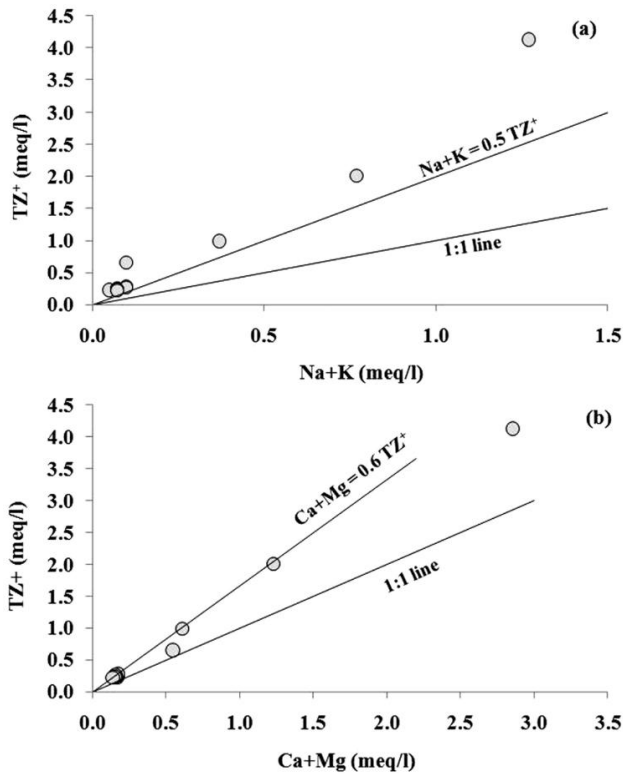


Fig. 3 — Covariance of: a) Na+K, and b) Ca+Mg; with total amount of cations of lake water of Schirmacher Oasis

were found mostly near to the $Na+K = 0.5 TZ^+$ line, indicating weathering of silicates by the inflowing melt water, contributing Na and K ions mainly, to the lake water. In addition, the $Ca+Mg$ vs total cations (TZ^+) plot (Fig. 3b) showed most of the samples along the 0.6:1 line ($Ca+Mg = 0.6 TZ^+$) indicating these ions also may be originated from silicate weathering.

Out of the 12 sampled lakes, a few (S3, S5, S8 & S12) were found to have $EC > 100 \mu S/cm$. To deduce the ionic chemistry of lake water, Gibb's diagram was plotted (Fig. 4). S8 was found to plot nearer to the rock-water dominance region than the others and S3, S5 and S12 were showing influence of evaporation from lake water concentrating the ions. The remaining lakes were found near to the precipitation dominance region.

Stable isotope composition

The stable isotope composition of the lake water of the Schirmacher Oasis is provided in Table 3. The observed δ values are typical for the Polar lakes, which receives substantial glacial melt water input. During the formation of ice, the heavier water molecules are preferentially added to the solid phase. Experimental studies have shown that for $^{18}O/^{16}O$,

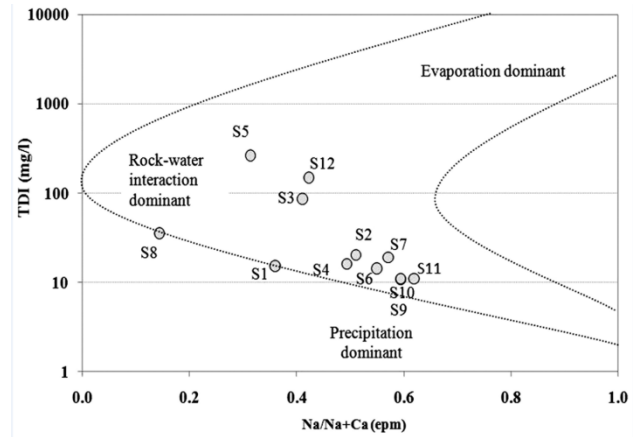


Fig. 4 — Gibb's plot of $Na/Na+Ca$ vs. TDI of lake water of Schirmacher Oasis

Table 3 — Stable isotopic composition of lake water in Schirmacher Oasis

Code	δD (‰)	$\delta^{18}O$ (‰)	d-excess (‰)
S1	-207.9	-25.3	-5.15
S2	-201.2	-24.3	-7.07
S3	-202.0	-24.0	-10.2
S4	-206.9	-24.7	-9.18
S5	-167.2	-18.0	-23.3
S6	-213.8	-25.1	-12.8
S7	-192.5	-21.2	-23.2
S8	-250.2	-31.2	-0.97
S9	-249.1	-30.9	-1.73
S10	-220.1	-26.6	-7.64
S11	-237.1	-28.6	-8.37
S12	-184.5	-19.3	-30.5

isotopic enrichment factor of ice with respect to water ($\alpha_{ice-water}$) range from 1.00291 to 1.0048 and for ($^2H/^1H$), it range from 1.0171 to 1.0212^(ref. 31). When ice is formed fast, the equilibrium fractionation values are still lower particularly for $^2H/^1H$ (1.017)^(ref. 32). Slightly lower values of $^2\alpha_{ice-water}$ (1.013 - 1.017) were observed in ice covers of lakes and rivers³³⁻³⁵. According to Souchez³⁶, the apparent fractionation factor for $^2\alpha_{ice-water}$ is roughly half the equilibrium value for water and ice. Horita *et al.*³¹ have shown that the stagnant diffusive layer in the liquid phase favouring the transport of lighter water molecules controls the transport of water molecules onto the bottom of the ice. Accordingly, the melt water will be depleted in heavier isotopes. Consequently, the equilibrium isotope fractionation at the ice-water interface is partly shifted favouring the heavy water molecules. This shifting depends on the rate of freezing and the extent of mixing of the water column. Hence, molecular diffusion controls the

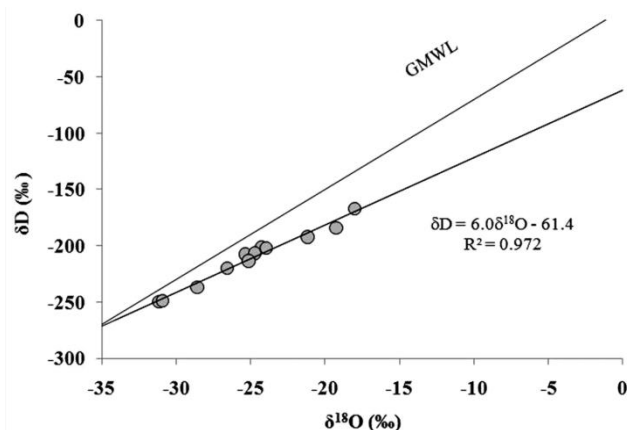


Fig. 5 — Regression plot of δD and $\delta^{18}O$ of lake water of Schirmacher Oasis (GMWL is also given)

transport of the water molecules in the boundary layer, the thickness of which determines the apparent ice-water isotope fractionation factor³⁷.

$\delta D - \delta^{18}O$ relationship

The δD and $\delta^{18}O$ values of lake water were found to plot below the GMWL with a slope of 6 in the regression plot (Fig. 5). As seen earlier, due to the diffusion controlled kinetic effect at liquid-ice interface, the formation of ice in lakes have a smaller isotope fractionation for $^2H/^1H$ (1.013 – 1.017), which results in a slope of 5-6. In addition, in some lakes, evaporative enrichment of water is evident from the higher ionic content. This is also confirmed by their relatively enriched isotopic composition. The evaporation of lake water can also lower the slope of the $\delta D - \delta^{18}O$ regression line.

The lake water samples can be grouped into two based on the isotopic composition as $\delta^{18}O < -20$ ‰ and $\delta^{18}O$ between -15 ‰ and -20 ‰. Most of the samples were found in the first group. Relatively enriched δ values were obtained for S5 and S12, in which ionic concentrations were also higher. Since the sampled lakes were shallow, evaporation in the austral summer may have concentrated the solutes and enriched the water in these lakes.

Conclusions

The lakes of the Schirmacher Oasis region of the East Antarctic region were explored to find the chemical and stable isotope compositions. The lakes were fresh water in character, which receives input from glacial melt water. The major geochemical processes can be the weathering of carbonate and silicate minerals and in some lakes, evaporation was

found to control the ionic makeup. The lakes were isotopically depleted and are characteristic of the polar lakes receiving glacial melt water. The kinetic fractionation effect at the ice-liquid boundary/evaporation of lake water determines the slope of the regression line of the lake water. Isotope data also affirmed the effect of evaporation from the shallow lakes during austral summer.

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Conflict of Interest

The Author(s) declare that there is no conflict of interest.

Author Contributions

The authors GG and RTR conceived the presented idea and interpretation of data; MP and MP carried out the analytical determinations and PSS and RR did the field work at Antarctica. All the authors have discussed the results and have contributed to the final manuscript.

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