Research Article

Chemical composition and isotopic signatures of ice and snow over a Himalayan Glacier (Satopanth) in India

A. S. Panicker[1,2] · K. Sandeep[1,2] · A. S. Gautam[3] · Naveen Gandhi[1] · G. Beig[1] · H. C. Nainwal[3] · P. S. P. Rao[1] · P. D. Safai[1] · S. Das[4] · V. Waghmare[1]

Abstract

This study reports the chemical composition and isotopic signatures of snow and ice over a Himalayan Glacier in India. An observational campaign was carried out from September 22, 2016, to October 2, 2016, over Satopanth in central Himalaya. The pH value of ice and snow, respectively, was 5.6 ± 0.4 and 5.9 ± 0.35 over the glacier, indicating moderate acidity of the glacier components. Calcium (Ca^{2+}) was the dominant component in snow (35.2%), while sulfate (SO_4^{2-}) was dominant in ice samples (52.7%). The neutralization factor was estimated to find the extent of neutralization of acidic fractions by basic components. It is found that Ca^{2+} was the prominent neutralizing factor both in snow and ice over the region. Oxygen and hydrogen isotopic analyses of snow, surface layer ice and debris-covered ice suggest that the moisture source is common for all three components. δD and d-excess values of snow at Satopanth are different than that of those for Chorabari, Dokriani and Tiprabank Glacier, indicating the plausibility of different sources of moisture for these glaciers. Limited observations suggest that the interaction of ice with the debris has no impact on the isotopic signatures of the ice over the region; such non-alteration of isotopic signatures makes the region important for ice core-based paleoclimatic studies.

Keywords Himalayan Glacier · Chemical composition · Snow and ice · Isotopic analysis

1 Introduction

The melting and retreat of glaciers due to global warming have been a major issue in the Himalayan region. Even though major portion of the glaciers in Himalaya are retreating, some portion are remaining stationary or advancing [3, 27, 39]. The dust particles present over glaciers have significant effect in controlling the glacier retreat. It is shown that the high loading of dust works as an insulator and moderates solar heating of the underlying surface [9]. The chemical composition of snow and ice over glaciers indicates the essential minerals and salts present in the glacier, which can account for the climatic and environmental changes [4]. The ionic deposition over glaciers are mainly contributed by circulation patterns and activities in the local environments [24]. Many glaciers in central Himalaya are featured with the covering of soil and stone debris over the ice surface. The climate responses of debris-covered glaciers are poorly understood [3]. It is suggested that debris-covered glaciers can withstand glacier retreat by 45–50% more as compared to the bare glaciers [3]. Since the last century, a number of attempts have been made by several investigators to study the various glaciological aspects of the Himalayan Glaciers (e.g., [6, 12, 17, 20, 23, 27–29], etc). However studies on ionic composition of snow/ice observations are limited, as most of the studies are oriented in the geological perspective over central Himalaya. Hence a campaign mode study was conducted

over debris-covered Satopanth Glacier during September 22, 2016, to October 2, 2016, in central Himalaya to cover the chemical aspects. The exploration was mainly focused on the measurements of aerosols and chemical composition of ice and snow over the glaciers. Isotopic analysis also has been carried out with the collected samples of ice and snow over the region. Stable isotopes of water are widely used in understanding the hydrological and paleoclimatic features (e.g., [36, 37]). Stable isotopic composition of ice/snow mainly depends on precipitation isotopic composition and gets modified with the base temperature of glacier. Further melting, percolation, snow drifting, evaporation and sublimation also alter the isotopic composition of ice. Despite such complications, δD and $\delta^{18}O$ contents of ice represent the climatic history of the region [2]. In the Indian Himalayan region, no altitude effect was observed in $\delta^{18}O$ of fresh snow collected from Changme-Khangpu, Nehnar, Chhota Shigri Glaciers [30, 31, 33]. It is reported that the glacial melt contribution from Gangotri Glacier at Devprayag is 11% [17]. The recent isotopic studies, reported dominance of westerly and monsoon sources during winter and summer, respectively, in the Chorabari and Dokriani Glaciers [21, 43]. Still, stable isotopic studies

for the Himalayan Glaciers are limited [13, 31, 32, 34, 42]. This paper exclusively presents the chemical composition of snow and ice and its isotopic signatures over Satopanth Glacier. The sample collection and data are explained in Sect. 2. Results in detail are discussed in Sect. 3 and summary is provided in Sect. 4.

2 Sample collection and data

The observations were carried out over Satopanth Glacier (30.7456°N, 79.3437°E; 3858 m ASL) in central Himalayas. Major portion of the Satopanth Glaciers are debris covered. The glacier is approximately 13 km long and 750 m wide. River Alaknanda, which is one of the major streams of river Ganges, originates from Satopanth Glacier. The location map of the observation site is shown in Fig. 1. The meteorological features of different central Himalayan Glaciers are described elsewhere [22]. The monsoonal time mean temperatures were found to range between 2.5 and 9.5 °C in different glaciers over the region. While maximum temperature was up to 14.7 °C, minimum temperatures ranged between − 3.4 and 6.1 °C. The relative

GMTED2010 30-arc-second topography height (meters MSL)

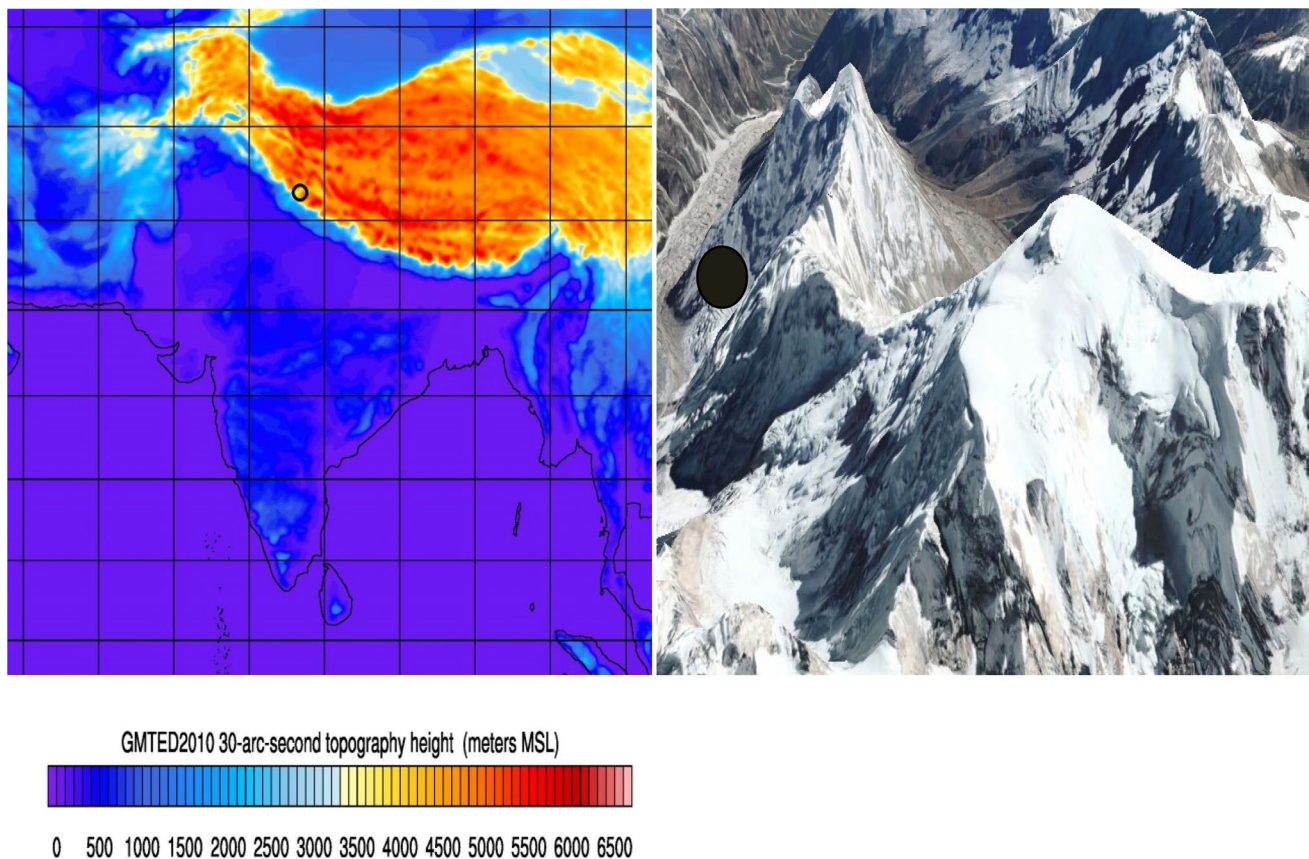0   500 1000 1500 2000 2500 3000 3500 4000 4500 5000 5500 6000 6500

Fig. 1 Location map of Satopanth Glacier (observational base camp highlighted with Google Earth)

humidity varied between 68 and 91% during monsoon seasons, and the wind speed was 2.3 to 10 km/h over the region. Thermally driven valley wind system was found to influence the intensity of winds and transport of pollutants over the region [22]. The sample collection of ice and snow was carried out on September 24 and 26 and October 1, 2016, in three different locations over the glacier. Due to the adverse weather conditions and time constraints, sample collection was possible only in these 3 days and could not separate fresh and old snow in the samples. Further, regarding isotopic data, this is a preliminary study for the Satopanth Glacier and showing limited isotopic data for a very short time period, collected randomly at glaciated region with the aim of exploring the region for paleoclimatic and moisture source studies. pH of the samples were measured using a pH meter (Eigenbrodt Gmbh Inc.). The details of pH meter are available elsewhere [38]. We have used Metrohm 850 professional ion chromatography (IC) system for the ion analysis. A sample processor is used to introduce samples for inline sample preparation. After the preparation of sample, the sample solution is introduced through a sample loop on the injector in to the device system. The sample is pumped on to the column by the eluent, and ions in the samples are attracted by stationary phase of the column [40]. The solution then go through the conductivity detector and interprets peak in the chromatogram for respective cations and anions. A detailed description of ion chromatograph and its working principle is available elsewhere [26, 38].

Oxygen and hydrogen isotopic analyses of the snow and ice samples were carried out using a LGR isotopic water analyzer (Model: TIWA-45-EP; [7]). These analyses yielded simultaneous δD and $\delta 18O$ isotopic data through high-resolution laser spectroscopy that quantifies concentrations of individual isotopologues of H_2O and calculates isotopic ratios [16, 25]. Using the LASER absorption property, the stable isotope ratios are measured directly based on the molecular mass dependency of the individual absorption lines. The autosampler is used to inject water sample from the sample vial using 1.2 μL syringe to an injector block (vaporization chamber) heated at 70 °C which is connected to the analyzer. A Teflon tube is connected to the pre-evacuated (using pump) optical cavity. For each sample and calibrated standard, nine injections are measured and average values are reported. The precision of the hydrogen and oxygen isotopic measurements was better than 1.0‰ and 0.1‰, respectively. Accuracy of the analyses was monitored through isotopic measurement of International (USGS-46 and USGS-47) and our in-house lab standard (IITM-A) standards. The conventional δ notations are presented with reference to V-SMOW (Vienna standard ocean water), in this study, the *d*-excess values for the samples are estimated as $(\delta D-8 \times \delta^{18}O)$ [8].

3 Results and discussion

3.1 Chemical composition of snow and ice

The samples of ice and snow were analyzed for chemical composition using an IC as explained in Sect. 2. The average pH of ice samples was found to be 5.6 ± 0.4, and the snow samples showed a pH of 5.9 ± 0.35. This indicates the moderate acidic nature of both snow and ice over the region. However, mild alkalinity was reported over another central Himalayan region [20, 23]. A pH of 6.1

Fig. 2 Chemical composition of ice samples (in mg/l) over Satopanth Glacier
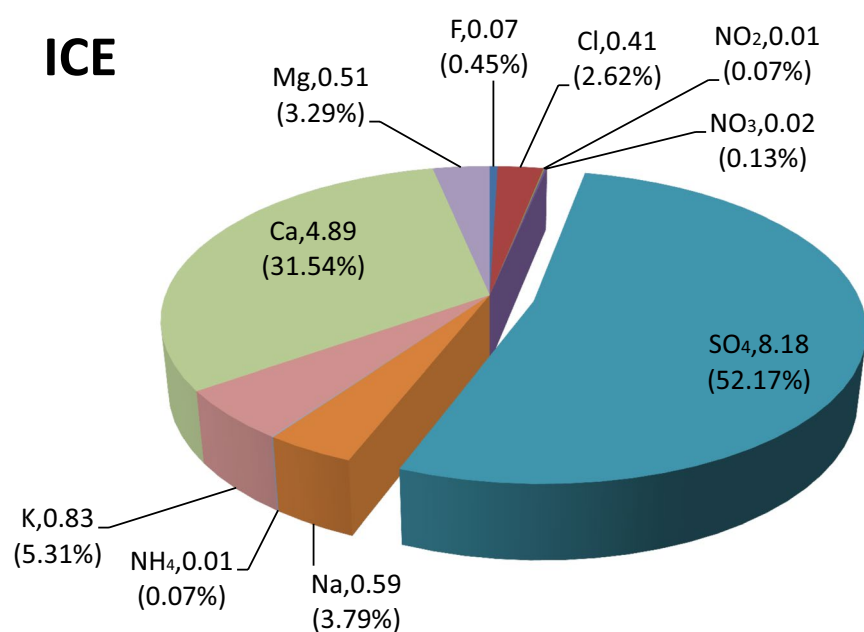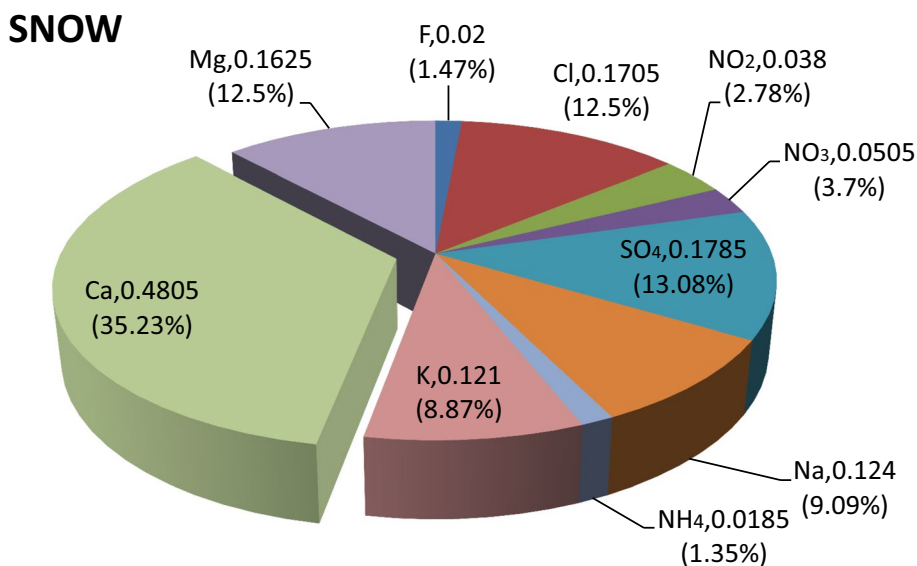
Fig. 3 Chemical composition of snow samples (in mg/l) over Satopanth Glacier

for snow was reported over Antarctica [1]. The chemical composition of ice is shown in Fig. 2. Sulfates were found to be the major contributor in ice samples (52.71%). The respective contribution of available components in ice was $SO_4^{2-} > Ca^{2+} > K^+ > Na^+ > Mg^{2+} > Cl^- > F^- > NO_3^- > NO_2^{3-} > NH_4^+$. The lower pH in ice may be attributed to the higher presence of SO_4^{2-}. Ca^{2+} was found to be the second major component in the glacier ice. Ca^{2+} (31.6%), K^+ (5.32%), Na^+ (3.79%) and Mg^{2+} (3.29%) were other major contributors to ice. However, it may be noted that Ca^{2+} was the major component contributing up to 35.2% of snow samples (Fig. 3). SO_4^{2-} showed the second highest contribution to snow (13.1%). The respective contribution of chemical components in the snow was $Ca^{2+} > SO_4^{2-} > Cl^- > Na^+ > K^+ > Mg^{2+} > NO_2^{3-} > NO_3^- > NH_4^+ > F^-$. Presence of more Ca^{2+} might have led to comparatively less acidity of snow compared to ice. The major reason for sulfate contribution was reported to be industrialization [10]. The natural reasons for excessive sulfate in ice could be due to the transported sulfur and its oxidation and to sulfate, which gets deposited by precipitation over the region [41]. Other natural sources of sulfates in the soil debris could be the sulfate bearing minerals like gypsum and oxidation of sulfide mineral like pyrite present over the region [11]. The anthropogenic contribution could be due to the deposition of long range transported sulfate aerosols over the region [44]. As natural sources for sulfates such as marine air mass and vegetation emission hardly contribute over the region, the higher sulfates could be transported from adjacent areas of Mana or Badrinath due to anthropogenic activities such as cooking or vehicular transport. The larger concentration of SO_4^{2-} and Ca^{2+} in Himalayan region are attributed due to vehicular traffic and biomass burning

over the region [38]. Other reason for sulfate concentration could be explained by aqueous-phase oxidation of SO_2^{2-} in clouds and prominent gas to particle conversion processes [35]. Na^+ (9.09%), K^+ (8.87%) and Mg^{2+} (11.91%) were found to be the other major contributors in snow over the region. Soil is reported as the major sources of the above components [35]. Like sulfates, one major source for excess calcium in snow could be the dust present in debris. It is reported that dust is a major contributor of Ca^{2+} [35]. Calcium in these areas is mainly of crustal origin and Ca^{2+} could be found in lime /calcium carbonate, dolomite, etc. of subsiding soil [14, 41]. The mass of sulfates and calcium in ice was almost 10–45 folds higher than that over snow. It suggests that the long time mixing of debris with ice is a more prominent source of the minerals in ice compared to deposits of relatively new snow. Another central Himalayan chemical composition study showed the concentration order as follows $Ca^{2+} > Cl^- > Na^+ > SO_4^{2-} > HCO3^- > NH_4^+ > NO_3^- > Mg^{2+} > K^+ > F^-$ in the fresh snow [20, 23]. Chemical composition data over Chhota Shigri glacier of central Himalayas is well documented [34]. It showed that K^+ and Ca^{2+} have mostly terrestrial sources, but Mg^{2+} has both marine and terrestrial source connection. It is found that southwest monsoon rain increases weathering of glacial debris and produce more sulfate ions (SO_4^{2-}) in snow and ice [15].

3.2 Neutralization factors

The lower pH of ice (5.6) and snow (5.9) suggests that the glacier environment is moderately acidic. To reduce the escalation of acidity, basic components plays vital role. To estimate the neutralization of such acidic components

such as SO_4^{2-} and NO_3^- by basic components, neutralization factors were estimated (mainly for Ca^{2+}, Mg^{2+} and K^+) over Satopanth. Another major alkaline component NH_4^+ was not considered due to its very meager contribution to the total composition. To avoid the contribution of potential transported less neutralizing sea salt fractions, we calculated

$$nss \; X = X_{(in \; sample)} - [X/Na_{(in \; sea)} * Na_{(in \; sample)}]$$

The non-sea salt fraction (sea salt fractions of anions could be transported to the area by monsoon winds and can be deposited on glacier surface). The neutralization factors are estimated according to the methodology suggested elsewhere [19]. Non-sea salt fraction (nss) was computed considering Na as reference component for sea source and using standard seawater ratios [18]. Accordingly, NF values for Ca, Mg and K were calculated as:

$$NF(Ca) = nss \; Ca/NO_3 + nss \; SO_4$$

$$NF(Mg) = nss \; Mg/NO_3 + nss \; SO_4$$

$$NF(K) = nss \; K/NO_3 + nss \; SO_4$$

The neutralization factors are tabulated in Table 1. It is found that Ca^{2+} is the prominent neutralizing agent of acidity and keeping the escalation of acidity in limits. The neutralization was found to be of the order $Ca^{2+} > K^+ > Mg^{2+}$ for both snow and ice. The NF was 0.05 for Mg^{2+}, 0.09 for K^+ and 0.6 for Ca^{2+} in ice. NF, respectively, was 0.795, 0.63 and 2.57 for Mg^{2+}, K^+ and Ca^{2+} in snow. The lower acidity in snow could be attributed due to the higher neutralization by Ca^{2+}. However, comparatively lower NF in ice could be reason for enhanced acidic nature of ice samples.

3.3 Isotopic analysis

The isotopic analysis of the samples has been carried out as described in Sect. 2 for surface layer ice, debris-covered ice and also for snow samples. As stated earlier, this is a preliminary study with limited isotopic data for a very short time period collected randomly at glaciated region. Here, we present δD and $δ^{18}O$ data (Table 2) for fresh snow, accumulated surface ice and ice from debris collected over the Satopanth Glacier. Surface ice isotopic values $δ^{18}O$ (δD) −14.5‰ (−94.2‰) from the Satopanth Glacier are very

Table 1 Neutralization factors of different components in snow and ice samples

	NSS (ice)	NSS (snow)	NF (ice)	NF (snow)
K^+	0.385392	0.116412	1.056592	0.627558
Ca^{2+}	0.717558	0.475788	1.96726	2.564895
Mg^{2+}	0.09717	0.14762	0.266402	0.795795

Table 2 Sample details and their δD and $δ^{18}O$ values with d-excess

Name	δD (‰)	$δ^{18}O$(‰)	d-excess
Snow	−92.4 ± 0.16	−14.1 ± 0.05	20.3
Surface ice	−94.2 ± 0.09	−14.5 ± 0.03	21.4
Debris-covered ice	−86.1 ± 0.11	−13.3 ± 0.09	20.5

close to that of reported [$δ^{18}O$ (δD) − 13.51‰ (−91.2‰)] for similar altitude 3905 m a.s.l. of Tiprabank Glacier [34]. However, different d-excess values (21.4 for Satopanth Glacier versus 16.9 for Tiprabank Glacier) indicate the different moisture sources at both the glaciers. It is shown that the westerlies are the main source of moisture of snow in Chorabari and Dokriani Glaciers during post-monsoon and winter [21, 43]. $δ^{18}O$ (δD and d-excess) values of the present study are similar to that of snow collected during September–October from Chorabari and Dokriani Glaciers, suggest the similar source of moisture, i.e., westerlies at Satopanth as well. The surface ice isotopic signatures are slightly depleted with respect to the fresh snow at the Satopanth Glacier. The depletion in the surface ice indicates slightly cooler temperature conditions during the time of accumulation of ice. However, similar d-excess values of snow, ice and ice from debris suggest that the moisture source is common for all. Evaporation and sublimation processes are plausible reasons of the enriched isotopic values of ice collected from debris. However, no alteration of d-excess suggests that the interaction of ice with the debris has no impact on the isotopic signatures of the ice. Presence of carbonate minerals influence isotopic values of ice by interacting ice through physical–chemical reactions and hence change isotopic signature of accumulated ice. However, similar isotopic values of surface ice and ice associated with debris do not alter isotopic values of surface ice. This is because the region is dominated by granite-granodiorite and low in carbonate [5]. Further it could also be concluded that evaporative effect is minimum once ice gets accumulated in the region as the region remains under very low temperature throughout the year. Such non-alteration of isotopic signals in snow and ice of the Satopanth Glacier shows the importance of the region for paleoclimatic studies related to past temperature reconstructions, variability in moisture sources, glacier moments, etc.

4 Summary and conclusion

A campaign was carried out over Satopanth Glacier in Himalaya during September 22–October 3, 2016, periods to collect snow/ice samples for its chemical characterization and also to analyze its isotopic signatures. The pH

of glacier ice was found to be 5.6 ± 0.4, and deposited snow was found to be 5.9 ± 0.35 over Satopanth Glacier. This indicates toward more acidity in ice. The SO_4^{2-} was the major contributor to ice (52.7%), whereas Ca^{2+} dominated in snow (35.2%) over Satopanth Glacier. Debris cover over glacier could be major source of calcium than long range transport of the minerals. Estimates of neutralization factors revealed that Ca^{2+} component is able to neutralize and keep the acidity of ice and snow under check over the region. Oxygen and hydrogen isotopic analyses of snow, surface layer ice and debris-covered ice suggest that the moisture source is common for all three components in the glacier. It is also identified that the interaction of ice with the debris has no impact on the isotopic signatures of the ice. δD and d-excess values of snow at Satopanth are different than that of those for Chorabari, Dokriani Glaciers and Tiprabank Glacier, which indicates the plausibility of different sources of moisture for these glaciers.

The observations over Satopanth Glacier suggest that the snow samples present over the glacier are less acidic compared to ice plausibly due to more neutralization of acidic fraction by dominance of Ca2$^+$ in snow. Limited observations over the glacier suggest that the interaction of ice with the debris has no impact on the isotopic signatures of the ice over the region such non-alteration of isotopic signatures makes the region important for ice core-based paleoclimatic studies. Hence, more exploration is necessary in Satopanth Glacier to unravel its changes in chemical and paleoclimatic aspects in the context of climate change.

Compliance with ethical standards

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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