Aerosol perturbations related to volcanic eruptions during the past few centuries as recorded in an ice core from the Central Dronning Maud Land, Antarctica

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High-resolution glacio-chemical analyses were carried out in a 62.2 m long ice core recovered from the Central Dronning Maud Land, East Antarctica, to evaluate temporal changes in environmental characteristics during the past five centuries. The sulphate (SO_4^{2-}) content within the core varied between 15 and 377 ppb, whereas the sodium (Na^+) and chloride (Cl^-) content fluctuated widely from 7 to 500 ppb and 25 to 1461 ppb respectively. The computed non-sea-salt sulphate ($nssSO_4^{2-}$) record reveals the existence of several outstanding peaks that can be attributed to the sulphate aerosol deposition during large volcanic events as recorded in Antarctica and elsewhere. Major volcanic events identified at the core site include: Mt Pinatubo (1991), Agung (1963), Krakatau/Tarawera (1883/1886), Tambora (1815) and Huaynaputina (1600) among several other moderate events. Comparison of our $nssSO_4^{2-}$ record with that of ice core records from Greenland reveals analogous sulphate deposition during certain major volcanic events, demonstrating the interhemispheric transport of aerosols during large volcanic eruptions. Relatively high Cl^-/Na^+ ratio throughout the core (mean 3.1) compared to that of the sea water ratio implies additional sources of Cl^-, most likely due to the intense scavenging of gaseous Cl^- in the lower atmosphere.

Keywords: Antarctica, glacio-chemistry, ice core, volcanic aerosol.

VOLCANIC eruptions inject large quantities of ash and gases into the earth's atmosphere, disturbing the chemical equilibrium of the atmosphere and affecting the planet's radiative balance and climate. Apart from water vapour, N_2 and CO_2, the most important injections to the atmosphere during a volcanic event[1] include the reactive gaseous compounds like SO_2, H_2S and HCl. Of these, sulphur-rich gases (principally SO_2) emitted during an eruption are the most important, that can subsequently react with hydroxyl radicals and other oxidants in the atmosphere, transforming quickly into H_2SO_4 aerosols[2]. Once injected to the stratosphere, these can cause the largest perturbation on climate in the form of cooling of the earth's surface as well as providing a nucleus for various chemical reactions that can even lead to the stratospheric ozone depletion[3]. The low-latitude eruptions seem to have the maximum possibility to influence global climate as their aerosols can be transported to both the hemispheres. Although the material within the troposphere washes out quickly, aerosols reaching the stratosphere have relatively long residence time (> 1 year) and any stratospheric SO_2 injection within the tropics may take 1–2 years to reach the polar regions, depending on various other factors[1,3]. For example, the explosive eruption of Mount Pinatubo in 1991 – the most dominant volcanic event recorded in the past century – is estimated to have injected ~ 20 megatons (1 Mt = 10^{12} g) of SO_2 into the stratosphere and its sulphate signals were detected in the South Pole snow within ~ 2 years[4].

Changes in the amount and composition of atmospheric aerosol imprinted in the polar snow layers are related to changes in source, transport mechanisms, atmospheric removal processes and the extent, frequency and seasonality of snow accumulation rates, controlled by regional/global climatic variations[5]. In order to evaluate the climatic effects of volcanism, it is important to have reliable means to directly record the sulphate aerosol load in the stratosphere in the past[1,6]. However, reliable direct measurements of sulphate aerosol loading were possible mainly during the past few decades of satellite availability and ship-borne measurements. A recent review of aerosol ship-borne optical depth measurements over the ocean also provided important information on various aerosol distributions over the past 30 years[7]. However, in the absence of any such direct data before these periods, polar ice cores provide one of the best possible archives of past volcanic events since they reliably record the stratospheric sulphate aerosols that have direct relevance to the climate. Ice cores offer continuous,

highly resolved (annual to seasonal) long-term records of not only temperature and precipitation, but also atmospheric composition and transport. To trace the volcanic events in the ice core and the stratospheric aerosol loading related to it, rapid methods like electrical conductivity (ECM) and dielectric profiling (DEP) have been extensively used by various workers[8–11]. Apparently, these methods are not faithful proxies for the stratospheric sulphate aerosol loading due to the following: ECM detects the ice acidity and includes acids other than H_2SO_4 (HNO_3, HCl, HF, etc.), whereas the DEP is an indirect measurement of total salt content and acidity of the ice. Direct trace elemental analysis of the ice cores can provide a reliable measure of specific aerosol loading related to volcanic events.

Antarctica being the vital link in climate studies and also the cleanest part of the earth's surface, ice cores obtained from this remote continent have been extensively studied to understand the natural events and past climate change[4–6,9–21]. Although several records are also available from East Antarctica, no systematic glacio-chemical data were available from the Central Dronning Maud Land (CDML) region. Considering the lack of data in this region, India initiated shallow-to-medium depth ice-core drilling activity in the proximity of Indian station Maitri, under physically and logistically challenging conditions[22,23]. The initial data from this region indicated the utility of ice cores as high-resolution archives of climate change and extreme events during the past century[11]. In order to better understand the temporal and spatial variations in the glacio-chemistry of the CDML region of Antarctica, systematic field and laboratory studies are being carried out since then. To accomplish this, a unique state-of-the-art facility was also established recently at the National Centre for Antarctic and Ocean Research (NCAOR), Goa, exclusively for the archival, processing and analysis of ice cores. The present report deals with the glacio-chemical profiles of an ice core collected from CDML and its implications to the volcanic events that occurred during the past ~ 500 years.

Material and methods

During the 22nd Indian Antarctic Expedition, a 62.2 m long ice core (IND-22/B4) was recovered from the continental ice sheet at 70°51.3′S and 11°32.2′E, near the Tallaksenvarden nunatak of CDML (Figure 1). Ice core drilling was carried out using an electromechanical drilling system (diameter ~ 10 cm) during the polar nights of the austral summer (February–March 2003; Figure 2). The cores were labelled and packed in good-quality polythene containers and were subsequently shipped in deep-freezer facilities to NCAOR. The ice core samples were scientifically archived in frozen conditions (– 20°C) in custom-made expanded polypropylene (EPP)-insulated containers at the NCAOR cold-room facility, till further processing. In the processing laboratory (–15°C), the ice cores were first

manually decontaminated by removing a thin outer layer using contaminant-free microtome blades and subsequently sub-sampled using custom-made bandsaw machines. Extreme care was taken to minimize contamination problems during processing and all tools and containers was precleaned. To improve the quality further, only the inner core of the samples was used for chemical analysis. Prior to chemical analysis, the samples were melted at room temperature in a Class 100 clean room.

Major soluble anions (SO_4^{2-}, Cl^-, NO_3^-) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+) were measured in the melted ice samples using ion chromatographic techniques in a Class 100 clean room. Ion chromatographic analysis of samples was carried out using Dionex™ ICS-2500 system equipped with an automated EG50 Eluent Generator Module and a CD25 conductivity detector. Cations were separated on an IonPac CS17 (4 mm) column with methanesulphonic acid (MSA) as eluent at a flow rate of 1.0 ml/min, using the gradient method and an IonPac CG17 Guard column with a CSRS-ULTRA Cation Self-Regenerating Suppressor. The anions were separated on an IonPac AS11-HC (4 mm) column with potassium hydroxide at 1.2 ml/min as eluent, using the gradient method and an IonPac AG11-HC Guard column, with an ASRS-ULTRA (4 mm) Anion Self-Regenerating Suppressor. The sample injection volume on both the analyses was 100 μl.
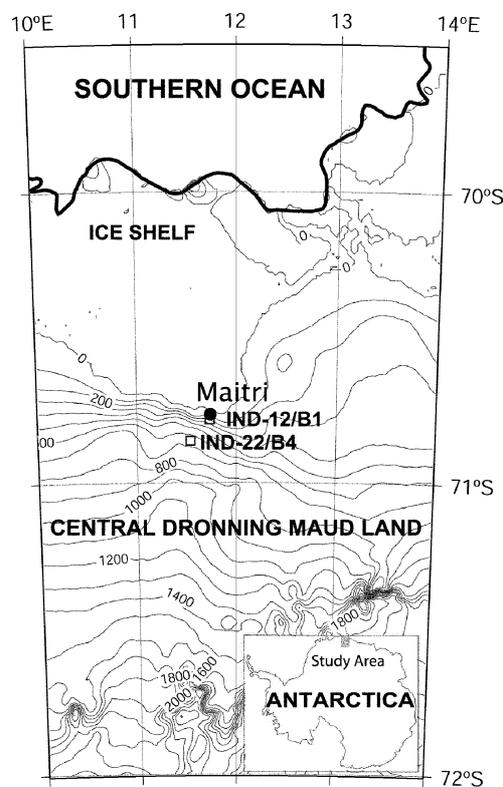

Figure 1. Study area and location of IND-22/B4 ice core within the Central Dronning Maud Land. IND-12/B1 denotes the core studied by Nijampurkar et al.[11].
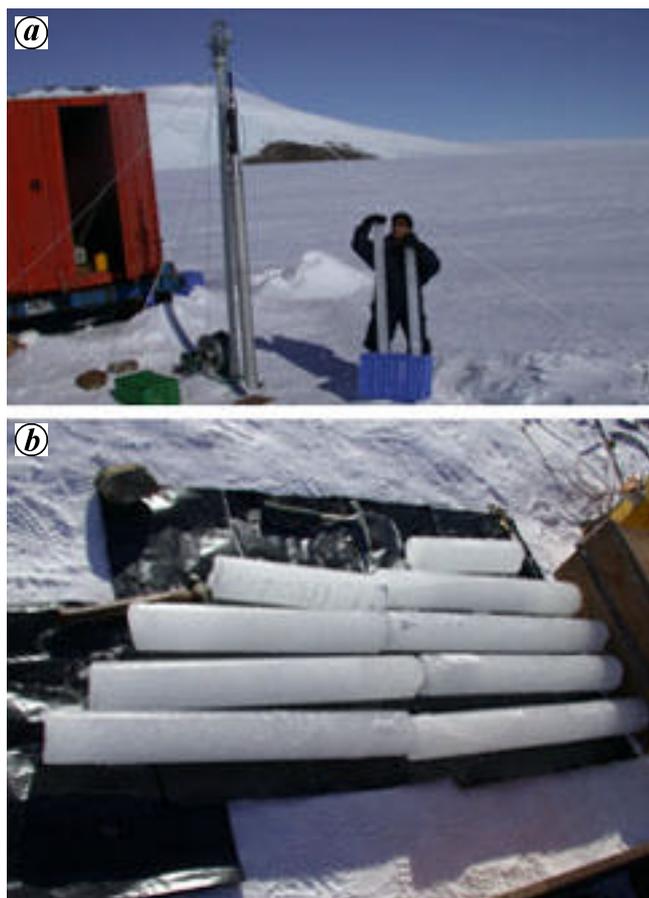
Figure 2. Field photographs showing (*a*) ice core drilling during the 22nd Indian Antarctic Expedition and (*b*) freshly drilled ice cores.

Figure 3. Depth profiles of SO_4^{2-}, Na^+ and Cl^- (all units in ppb or µg/l) and the Na^+ to Cl^- relation for the top ~50 m of the IND-22/B4 core. Numbers on the sulphate peaks denote volcanic events as given in Table 1.

Results and discussion

Sulphate content within the IND-22/B4 core varied widely between 15 and 396 ppb, with an average value of 95 ppb (Figure 3). There are several spikes in the sulphate data, which are similar to those demarked within several ice cores from Antarctica and elsewhere. Sulphate ion has mainly three sources in Antarctica: sea-salt spray, marine biological processes as well as from volcanic eruptions[24]. Of these, the most spectacular and anomalous signals are related to volcanic eruptions that can spew millions of tons of sulphate into the atmosphere and have high (few years) stratospheric residence time. In order to differentiate the sulphate signal related to volcanic eruption from that of the sea-salt-derived sulphate, the total sulphate concentration is normalized using sodium (Na^+) as reference species and using the sulphate-to-sodium ratio (0.252) in sea water[24]: $(nssSO_4^{2-}) = (SO_4^{2-}) - 0.252 \, (Na^+)$. It is well established[12] that Na^+ is the most reliable marker for sea salt compared to Cl^-.

Additionally, photo-oxidation of phytoplankton-derived dimethylsulphide (DMS) contributes to the background $nssSO_4^{2-}$ (non-sea-salt sulphate) signal, which in Antarctica is essentially controlled by the seasonal changes in marine productivity[13]. In order to separate the volcanic sulphate record from this 'noise', we have estimated a sulphate background for the core by adding the average value of the sulphate record as well as its standard deviation (Figure 4). Accordingly, the maximum $nssSO_4^{2-}$ background of the present record is estimated to be of the order of 125 ppb (Figure 4). This estimation is similar to the highly sensitive and robust estimation for the EPICA ice cores from Dronning Maud Land[14], and is much higher than the 'normal' background variations (55 ± 12 ppb) esti-

Calibration was done using standards from IV™ (Inorganic Ventures Inc.), USA. Standard solutions were prepared by dilution of individual standard stocks of 1000 ppm concentration with dilution chosen for different ions to be similar to those in ice samples by diluting using ultrapure (18.2 MΩ) water freshly obtained from a Millipore™ (Milli-Q Element) system. A blank analysis was also made using Milli-Q water. All reagents used were of ultra-pure grade and extreme care was taken to pre-clean all glassware and other labware using fresh Milli-Q water. Concentrations of NH_4^+, Ca^{2+}, K^+ and Mg^{2+} were extremely low near the detection limit of the system and therefore, were not used for interpretation. In order to confirm the quality of measurements, analysis of chemical standards was carried out on daily basis throughout the few weeks of analytical work. The present study will concentrate on the depth profiles of SO_4^{2-}, Na^+ and Cl^- in the top 50 m of the core to delineate the volcanic aerosol events in the recent past. Precision estimates for all ions reported here based on the repeated analysis of international chromatographic standards are better than 20 ppb.
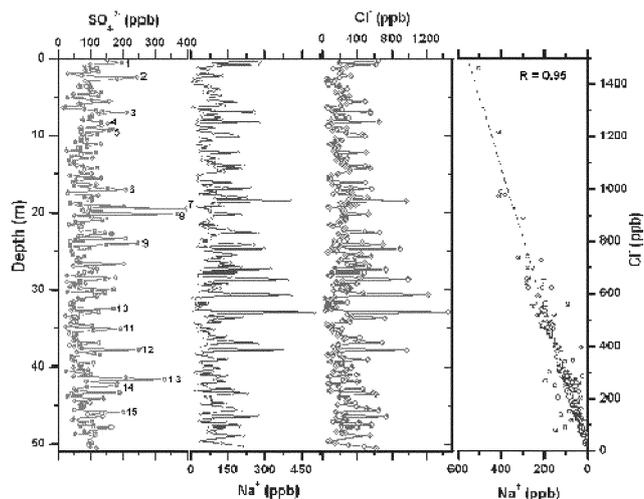
mated at the South Pole[15]. Therefore, we believe that our background sulphate estimation is the upper limit possible ('high') for this region. Peaks above the 'high' sulphate background within the $nssSO_4^{2-}$ profile of the core are, therefore, interpreted here as directly related to the volcanic eruptions in the past.

Preliminary volcanic chronology

Although long-term stake measurements of snow accumulation rates could not be carried out at the core site, accumulation rates at a nearby site (70°47′S and 11°44′E) in the CDML area are estimated to be between 12.5 and 26.6 cm/year[11]. Since no absolute dating control is available at present, we employed an indirect method using volcanic marker horizons. Volcanic chronology developed using measurements of ECM, DEP and $nssSO_4^{2-}$ have been extensively used for dating ice cores for the past millennium[8,9,16]. In fact, several $nssSO_4^{2-}$ ice core profiles from Antarctica and Greenland have shown the immense utility of $nssSO_4^{2-}$ records as a reliable marker for volcanic events as well as to develop a volcanic chronostratigraphy for ice cores[6,10,14,17–20].

In order to assign a preliminary volcanic stratigraphy for the present core, the highest sulphate peak at a depth of 19.54 cm was assigned to the Tambora (Indonesia) eruption of AD 1815, which was the most characteristic and dominant volcanic event reported in recent history (Table 1). Considering the estimated 1–2 years lag between the tropical eruptions and stratospheric aerosol transport to the

poles[19], the Tambora event in the present ice core record may be placed at 1816 ± 1 yrs AD. Further, we confirmed this as the Tambora event using the associated older event at 20.14 m (Table 1; Figure 4). Such a doublet of $nssSO_4^{2-}$ peaks has been widely reported from all Antarctic ice core profiles and used as one of the most reliable marker horizons for the past millennium[9,14,17–21]. The older peak was dated six years prior to the Tambora and was ascribed to an unknown eruption (hereafter called 'Unknown'), that left strong signals in the Antarctic and Greenland ice records contemporaneously, making the prominent sulphate doublet as an interhemispheric marker horizon[3,25].

With the understanding that the above doublet of sulphate peaks originated from the Tambora (1815) and the Unknown (1809) eruptions respectively, we can linearly interpolate to obtain a timescale, assuming a more or less constant accumulation rate. The average accumulation rate thus obtained was about 10 cm/yr. By comparing our sulphate records with the well-known indices of past volcanic events, we improved the chronologic constraints of our core through assignment of some of the notable $nssSO_4^{2-}$ peaks to the well-known volcanic events from the Antarctic ice cores (Table 1). The preliminary volcanic chronology thus proposed for the ice core is subjected to absolute dating in future and will be augmented using radioactive dating methods and high-resolution oxygen isotope analysis.

Identification of volcanic aerosol signals

Since the speed and direction of aerosol dispersals are influenced by the prevailing atmospheric processes, temporal variations in volcanic signals in the ice cores may reflect the changes in atmospheric circulation[19]. The prominent spikes detected above the 'high' $nssSO_4^{2-}$ background within the record of core IND-22/B4 suggest several significant volcanic events that may have had global or at least regional implications (Table 1; Figure 4). It is well known that only the volcanic eruptions south of 20°N lead to any significant sulphate input to the Antarctic region, due to the unique atmospheric circulation patterns[9]. In order to qualify the $nssSO_4^{2-}$ peaks as due to volcanic eruption, we used the internationally adopted criteria in other Antarctic ice core studies[6,18–21]. Thus we have made an attempt to report all significant volcanic signals that have been recognized from other Antarctic ice cores. However, as discussed earlier, we selected only those peaks that have an amplitude above the threshold value of 125 ppb, to be confident in our interpretations. We refrain from describing few peaks that were not documented well, even if few isolated ice-core studies report them.

While detecting various volcanic events, we have compared and contrasted our nss-sulphate data with the recent ice-core data from Antarctica[9,14,18–21]. We also compared our data with the available indices of past volcanic aerosol
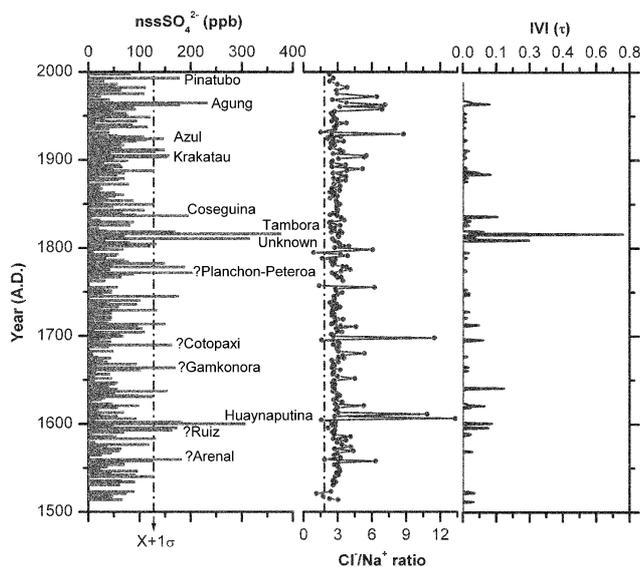

Figure 4. Non-sea-salt sulphate ($nssSO_4^{2-}$) and Cl^-/Na^+ profiles of the IND-22/B4 core with reference to the Ice core Volcanic Index (IVI) data. Vertical dashed line on $nssSO_4^{2-}$ record is the upper limit defined for biogenic sulphate and that on the Cl^-/Na^+ profile is the sea water Cl^-/Na^+ ratio (1.82). Note that the IVI data are the estimated optical depth (an index for the volcanic aerosol loading) synthesized from ice core sulphate data from Antarctica[6].

Table 1. Non-sea-salt sulphate concentration at selected depth intervals of core IND-22/B4 and volcanic events inferred from the record. The Volcanic Explosive Index (VEI) and Ice core Volcanic Index (IVI) are given for comparison (see text for details)

Peak no.	Core depth (m)	nssSO$_4^{2-}$ value (ppb)	Volcanic event assigned	Latitude	Year of eruption (AD)	VEI	IVI (t)	Reference
1	0.5	178	Pinatubo, Philippines	15°N	1991	6	na	4, 10, 14, 21
2	2.5	233	Agung, Indonesia	8°S	1963	4	0.12	4, 9, 14, 17–21
3	7.1	147	Azul, Chile	36°S	1932	5	–	10, 14
4	8.4	148	?Colima, Mexico	19°N	1889	4	–	14
5	9.4	154	Krakatau, Indonesia	6°S	1883	6	0.13	6, 9, 10, 14, 17–20
6	17.0	195	Coseguina, Nicaragua	13°N	1835	5	0.16	14, 19, 21
7	19.5	377	Tambora, Indonesia	8°S	1815	7	0.72	1, 3, 9–11, 14, 17–21
8	20.1	315	Unknown		1809		0.30	1, 3, 9–11, 14, 17–21
9	24.0	202	?Planchon-Peteroa, Chile	35°S	1762	4		10, 14
10	32.4	163	?Cotopaxi, Ecuador	0.6°S	1698?	3	0.09	14
11	35.1	170	?Gamkonora, Indonesia	1.4°N	1673	5?		10, 14, 19, 20
12	37.8	154	Mt Parker, Philippines	6.1°N	1641	6?	0.18	3, 14, 20
13	41.7	306	Huaynaputina, Peru	16.6°S	1600	6?	0.13	3, 10, 14, 18–21
14	42.2	173	Ruiz, Colombia	4.9°N	1595	4	0.11	14, 20, 21
15	45.9	181	?Arenal, Costa Rica	10.5°N	1525 ± 20	4		10, 14

loading of the atmosphere (Table 1). Of these, the Dust Veil Index (DVI) of Lamb[26] is based on the atmospheric impact observations after volcanic eruptions and is prone to error especially in Antarctica, where observational data are sparse. The Volcanic Explosive Index (VEI) of Newhall and Self[27], provides geologically inferred measure of the power of explosion as a scale of dissipated energy. Although less subjective than the DVI, the VEI is fundamentally related to the solid material injected and not necessarily representative of the climate-sensitive stratospheric aerosols. Contrastingly, the Ice core Volcanic Index (IVI) was created from a suite of well-dated ice core records from each hemisphere[1,6] and is a quantification of volcanic sulphate aerosol loading denoted in optical depth at a wave length of 0.55 μm. Therefore, the IVI seems to be more valuable for reference in the present study (Table 1; Figure 4).

The first significant nss-sulphate peak (Peak 1; 178 ppb) at 0.5 m from the top should be related to a recent volcanic eruption (Figure 4). The well-known explosive eruption of Mount Pinatubo (Philippines, 15°N) in June 1991 and/or that of 1991 Cerro Hudson (Chile, 46°S) are the most likely causes for this sulphate peak. However, the Pinatubo eruption was the most dominant (injected ~ 20 megatons of SO$_2$) compared to the Cerro Hudson eruption (~ 2 megatons of SO$_2$) and the aerosol loading was mostly restricted to the troposphere[14]. The proximity of the Cerro Hudson to Antarctica may have led to an early deposition (advection via upper troposphere) of sulphate aerosols in Antarctica compared to a delay (long-range transport via stratosphere) in the case of Pinatubo aerosols[4]. However, in the absence of an absolute chronology and sub-annual sampling resolution, it is not possible to differentiate the relative contribution of these two eruptions in the present study. The Pinatubo signal was widely reported from several recent firn/ice cores and snow pits from the East Antarctica[4,10,14,21].

Although it is well known that there was a major volcanic eruption of El Chichón (Mexico, 17°N) in 1982, sulphate signals are not evident in our records. In fact, such a scenario is also supported by studies on perturbations in the mean annual optical depth (visible, l = 0.55 μm). It was found that the estimated optical thickness of El Chichón compared to the Pinatubo (1991) and Agung (1963) was minor in Southern Hemisphere than it is in the Northern Hemisphere[3]. Satellite observations indicated that although the Pinatubo and El Chichón[28] eruptions are separated by only 2° of latitude, the El Chichón clouds extended till 30°N compared to that of Pinatubo which hovered around the equator, suggesting the influence of the prevailing wind pattern at the time of eruption on the volcanic aerosol distribution.

A strong peak (Peak 2) at 2.5 m depth appears to be originating from the 1963 Agung eruption (Indonesia, 8°S). The Agung episode with a VEI of 4, is one of the best-identified volcanic events in Antarctic ice-core records[4,9,14,17–21]. The widespread discovery of this event makes it an ideal time marker for the entire Southern Hemisphere. Following Karlöf et al.[10], Peak 3 is attributed to the Cerro Azul (Chile) eruption in 1932. Although this event has been assigned a VEI of 5, the sulphate signal is not very strong (Figure 4). It was suggested that the unusually low sulphur loading of the eruption could have been responsible for the poor detection of this signal in Antarctica and elsewhere[14]. This supports the argument that VEI is only a geological measure of the explosivity of the eruptions and not the sulphate input to the stratosphere[6]. The broad peak (Peak 5) at 9.2 m depth of the core may be due to the 1883 Krakatau (Indonesia, 6°S) and/or the 1886 Tarawera (New Zealand, 38°S) volcanic eruptions in the southern hemisphere (Table 1). Both the events are well recorded in history as well as in Antarctic ice core records[6,9,10,14,17–20]. However, considering the low sampling

resolution and because the Krakatau event is considered to be much greater and had a global impact[14,18], we assign Peak 5 as primarily due to the Krakatau fallout. Apparently, the aerosols injected to the atmosphere during the Krakatau eruption had less sulphur content[29]. This explains the relatively diminished sulphate signal in the present ice core during this time period. The Coseguina (Nicaragua, 13°N) eruption of 1835 also seems to have its imprints in our core, as an enhanced sulphate peak (Peak 6) at 17 m depth (Table 1).

As discussed earlier, the most prominent doublet of $nssSO_4^{2-}$ peaks (Peaks 7 and 8) is related to the Tambora eruption of AD 1815 and an older eruption attributed to an unknown volcano during 1809. During the Tambora event, the $nssSO_4^{2-}$ value in our core went up to 377 ppb (Figure 4). Tambora is considered to be the greatest volcanic event during the past 500 years, having a VEI of 7 and IVI[6] of 0.72. The global sulphate fallout related to this mega event was estimated to be as high as ~ 150 megatons (1.5×10^{14} g), making it one of the most impressive volcanic events that had direct climatic impact[29]. Although not documented in historical observations, considering the large sulphate signal in all ice cores, the 1809 event also must have had significant global impact. Physical evidence of glass shards also confirmed the presence of this event together with the Tambora eruption[30]. The 1809 event is a valuable time marker because of its presence in both the polar records, suggesting that the origin of this event must have been related to huge tropical eruption located somewhere in the tropics[19] between 20°N and 20°S. However, it is perplexing that an event of such a great magnitude was not recorded in the history.

A couple of peaks are observed around 24 m, of which Peak 9 has $nssSO_4^{2-}$ values reaching up to 202 ppb (Table 1; Figure 4). Although not comprehensible, following Karlöf et al.[10] and Traufetter et al.[14], the peak may be related to the Planchon-Peteroa (Chile) eruption of 1762. Peaks 10 and 11 may be attributed to the 1698 eruption of Cotopaxi (Ecuador) and the 1673 Gamkonora (Indonesia) eruption respectively[10,14,19,20]. Peak 12 at 37.8 m in our record can be attributed to an eruption in 1641. Although this event was previously thought to be due to the Awu (Indonesia) eruption[10,19], recent studies confirmed its origin from the Mt Parker (Philippines) eruption[14,20].

Based on comparison with other cores from Antarctica and after assuming a nearly constant accumulation rate, the remarkable $nssSO_4^{2-}$ peak (306 ppb, Peak 14) at 41.7 m depth is assigned to the Huaynaputina (Peru) eruption of AD 1600 (Table 1, Figure 4). It is known to be a great eruption, with the magnitude of eruption efficiency among one of the five largest historical eruptions[3,31]. Chemical analysis of the volcanic tephra found in the Antarctic ice also confirmed this event[30,31]. This is one of the most widely described[14,18–21,27] volcanic event in the Antarctic ice core, with a VEI of 6. A conservative estimate suggests at least 70 megatons global stratospheric sulphate loading

from the Huaynaputina eruption, making it one of the largest events that had significant climatic impact[3]. An older peak (Peak 14) at 42.2 m may be attributed to the Ruiz (Colombia) eruption of 1595, following available information from Antarctic ice cores[14,20,21]. Peak 15 at 45.9 m is tentatively attributed to the Arenal (Costa Rica) volcano of AD 1525 ± 20 after Traufetter et al.[14].

Interhemispheric comparison of volcanic signals

Most of the large volcanic eruptions within the tropical belt lead to significant aerosol loading to the stratosphere and have their imprints in both the hemispheres. It is therefore, useful to compare the impact of volcanic events identified in the present study with that of the Northern Hemisphere (especially Greenland) ice cores. A bipolar comparison of $nssSO_4^{2-}$ profiles during the past millennium using ice cores from Antarctica and Greenland had demonstrated strong correlation of the several prominent volcanic events[25]. Tambora is considered as the greatest volcanic event in the recent history that had its influence on both the hemispheres[6]. Assessment of our $nssSO_4^{2-}$ record with ice core records from Greenland and elsewhere, reveals comparable sulphate depositions attributed to the Krakatau (1883), Tambora (1815), Unknown (1809) and Huaynaputina (1600) events. Several moderate to small events found in the Antarctic records are absent in the Greenland ice records, suggesting that not all eruptions lead to dispersion of aerosols to both the hemispheres. It was suggested that moderate eruptions occurring at middle and high latitudes affect mostly the corresponding hemispheres[18]. Further, dispersal of aerosols into each hemisphere can be asymmetrical as a function of the time of the year, location of the Inter Tropical Convergence Zone as well as quasi-biennial oscillations (QBS)[3]. Because of such complexities, the Pintaubo eruption (15°N) was not reported from the Greenland records, although it is well recorded in all Antarctic ice core records. Variable transport of aerosols from an equatorial eruption into each hemisphere due to the stratospheric QBS, appears to produce different records in different regions.

Factors controlling excess-chloride record

Profiles of Na^+ and Cl^- exhibit a similar pattern within the core, with Na^+ values ranging from 7 to 500 ppb and Cl^- values varying from 25 to 1461 ppb (Figure 3). There exists a good correlation between Na^+ and Cl^- species, indicating that sea-salt aerosol is the major source of these ions in the study region. However, to differentiate the input of Cl^- from sea-salt aerosols and elsewhere, we computed the excess-chloride (excess-Cl^-) data by normalizing Cl^- data with Na^+ data in the core. The Cl^-/Na^+ profile thus obtained reveals large variations with values ranging between 0.5 and 13, having an average value of 3.1 (Figure 4). This is

substantially higher than the sea water Cl^-/Na^+ ratio (1.81), suggesting that additional sources of Cl^- are possibly important at the core site.

The exceptionally high Cl^-/Na^+ ratio (up to 13) at certain intervals in the core may indicate possibilities of large input of chloride to the atmosphere though volcanic degassing. However, enhanced Cl^-/Na^+ peaks are not comparable with the exceptionally high SO_4^{2-} content (Figure 4). Such a scenario is supported by earlier studies which suggested that unlike SO_4^{2-}, although large amount of Cl^- can be emitted during a volcanic eruption, the amount injected to the stratosphere is negligible[32]. This is because the volcanic plumes contain nearly 1000 times water content compared to Cl^-, leading to effective Cl^- scavenging due to rain induced by volcanic eruptions. It was advocated that such increased SO_2 levels at the ocean–atmospheric boundary during submarine volcanic events led to increased HCl production in the past[18]. The exchange reaction between sea-salt NaCl and atmospheric H_2SO_4 ($H_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2HCl$) may readily generate HCl. When this HCl is selectively deposited in the Antarctic snow, it can effectively increase the Cl^-/Na^+ ratio of snow. Although no significant eruptions have been recorded during the time intervals represented by the enhanced Cl^- levels of our core, it is possible that minor eruptions within the Antarctic realm and/or submarine volcanoes in the vicinity can lead to enhanced HCl and SO_2 emission to the lower troposphere.

The relatively high Cl^-/Na^+ ratio throughout the core is comparable to a South Pole record, wherein the chloride ions are enriched by ~ 40% relative to that of the sea water[33]. It was suggested that Cl^- enrichment in the South Pole is an indicator of aged sea-salt aerosol and long-range transport[34]. Considering the proximity of our core to the coast, the relatively higher Cl^-/Na^+ ratios throughout the core compared to the sea water ratio could be due to two factors: scavenging of gaseous HCl present in the air, and/or relatively low fractionation of sea salt particle during more intense circulation and shorter travel time. Further, it was observed that in Antarctica, the excess chloride and excess sulphate peak in summer (December and January), coinciding with enhanced biological production[35]. It was suggested that the sea-salt particles in the coastal Antarctic atmosphere can be modified by heterogeneous reactions with not only SO_2 and H_2SO_4, but also the volatile sulphur species (e.g. CH_3SO_3H, DMS and DMSO) derived from biological activity on the ocean surface during summer[36]. Therefore, we assume that the sea-salt aerosols probably play an important role as scavengers of acidic species, at least in the coastal Antarctic regions.

Conclusion

The major ion analysis of the IND-22/B4 ice core from CDML region in Antarctica reveals the existence of several outstanding peaks that may be attributed to large volcanic events as recorded in Antarctica and elsewhere. Interhemispheric correlation of the volcanic sulphate data using ice core records from Greenland and Antarctica reveals analogous sulphate deposition during certain major volcanic events like the Krakatau (1883), Tambora (1815), Unknown (1809) and Huaynaputina (1600) eruptions. High Cl^-/Na^+ ratio (mean 3.1) compared to that of the sea water implies additional sources of Cl^-, suggesting intense scavenging of gaseous Cl^- in the lower atmosphere. We propose that the sea-salt aerosols play an important role as scavengers of acidic species at least in the coastal Antarctic regions.

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