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GEOSCIENCES

Ionic and stable isotopic content in two Antarctic firn cores under different environment settings

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Abstract: This article compares isotopic, ionic and climatic data from two firn cores from the West Antarctic Ice Sheet (WAIS). The IC-02 (88°01’21.3”S , 82°04’21.7”W) and the IC-05 (82°30’30.8”S , 79°28’02.7”W) closer to the coast. The IC-02 had 488 samples analyzed covering 14.58 meters depth while the IC-05 had 602 samples analyzed covering 19.73 meters depth. The time interval for both ice cores is 25 years ranging from 1978 to 2003. Sodium, sulfate and chloride were analyzed via ion chromatography using three Dionex™ ionic chromatographers at the laboratories of Centro Polar e Climático (CPC) and at the Climate Change Institute. Stable isotope data was determined using cavity ring-down spectroscopy in a Picarro® spectrometer at the CPC. Annual accumulation was greater at IC-05 with an average of 0.35 m.eq.w.a^{-1} compared to 0.25 m.eq.w.a^{-1} at the IC-02. Stable isotope data was approximately 1.3 times more negative at the IC-02 which also presented higher d values. Na^{+} and Cl^{-} were in higher concentrations at the IC-05 however Cl/Na was greater in the IC-02. The Cl excess was found to be derived from fractionation of sea salt aerosols and not related to volcanism. This work presents new insights regarding the chemical differences between ice cores.

Key words: Antarctica, ice core, ionic content, stable isotopes.

INTRODUCTION

Global environmental changes have been observed and studied for the last few decades. However, in the recent years there has been a need for intensification of climate studies, instigating past and present climate investigations, and the modeling of climate scenarios for the future. Antarctica, for itself, has one of the best natural archives of the past climate. Its snow and ice provide numerous climate proxies. Due to its isolated geographic position, low temperatures throughout the year, low solar radiation incidence, and well-defined seasonality, some proxies significantly correlate with past climatic events (Legrand & Mayewski 1997, Mayewski et al. 2009, Simões 2011, Hou et al. 2013).

Hence, the chemistry of surface snow and firn and ice cores is important to investigate the past system, especially from samples from the last 300 years, crucial to understanding how anthropic activity impacts the climate and the chemistry of Earth’s atmosphere. The study of stable isotopes, mainly hydrogen and oxygen, is considered one of the most reliable proxies in studying past climate (Hou et al. 2013). Its application derives from water isotopic fractionation, which occurs with water molecule elements during thermodynamic phase transitions. Hydrogen has two stable isotopes: the ^{1}H (99.98% abundant) and the ^{2}H (or deuterium, D; 0.02% abundant). Oxygen has three stable isotopes: ^{16}O (99.757% abundant), ^{17}O (0.038% abundant), and ^{18}O (0.205% abundant), according to Holden et al. (2018). The first environmental-dependent fractionation studies were made by Dansgaard (1953) and Epstein & Mayeda (1953), which observed the influence of temperature in mid and high-latitude isotopic fractionation. A few years later, the same authors studied the isotopic variability along time in Antarctic and Greenland's ice cores (Daansgard et al. 1969, Epstein et al. 1970). Epstein et al. (1970) observed that the lower the temperature, the lower the deuterium and 18-oxygen proportions. The authors proposed that such variation could identify the summer-winter seasonal cycles, therefore, also dating the cores. However, deeper ice cores suffer post-depositional alterations that could affect the results (Dansgaard et al. 1969, Epstein et al. 1970). It is necessary then to use other dating methods, such as age markers events (i.e., reference horizons), to assess whether the record keeps an isotopic - local air temperature relationship with statistical confidence (Masson-Delmotte et al. 2008). From the 1990s, the stable isotope technique improved, and some methods to infer paleotemperature were developed (Jouzel 2013).

The ionic content of an ice core can also reveal important regional climate characteristics. The different ions that can be found in ice are deposited alongside the snow when the precipitation occurs (wet deposition) or by aerosol decanting in low snow precipitation regions (dry deposition), which takes place mainly in the interior of the Antarctic Plateau (Cuffey & Paterson, 2010). The snow ionic content and aerosols on the continent are influenced directly by air currents, which carry maritime ions, continental ions from nearby mountains, or other continents. The ionic content, therefore, can be used as proxies to identify environmental settings such as altitude, ocean proximity, humidity, source areas for air currents, etc. (Cunningham & Zoller 1981, Legrand & Delmas 1984, Legrand & Mayewski 1997, Rothlisberger et al. 2002, Curran et al. 2003, Trevena & Jones, 2006, Wolff et al. 2006, Abram et al. 2013).

This work examines how some variables (stable isotope ratios, ionic content and net annual accumulation), used as proxies for past climatic and environmental conditions, varied in two shallow firn cores collected at sites under different environmental conditions. One of these cores was taken from the East Antarctic Ice Sheet Plateau (EAIS), the other from the lower and warmer West Antarctic Ice Sheet (WAIS). These cores were recovered during the 2004-2005 Chilean-Brazilian crossing from Chilean station Tenente Parodi in Patriot Hills (Figure 1) to the US South Pole Amundsen-Scott station. This traverse contributed to ITASE (International Trans-Antarctic Expeditions), whose main objective has been to obtain data on the spatial and temporal climate and environmental variability of Antarctica in the last 200 years, using snow and ice cores. These include variations in major atmospheric phenomena such as ENSO, snow accumulation and extreme events such as volcanic eruptions.

MATERIALS AND METHODS

Area of study and sampling procedure

Both cores were drilled without drilling fluid, using a 3 inches FELICS (Fast Electromechanical Lightweight Ice Core System) drill. The drilling machine parts which touched the firn are made of anodized aluminum, stainless steel, polyethylene, and polyoxymethylene (Tavares 2020). Each recovered core section was weighted immediately after recovering, using a balance Bioprecisa BS3000A with 0.1 g precision. Then, the cores sections were put into polyethylene tubes and stored inside reinforced polystyrene boxes to maintain the low temperature. During all the traverse, the temperature inside the boxes was kept below -20°C.

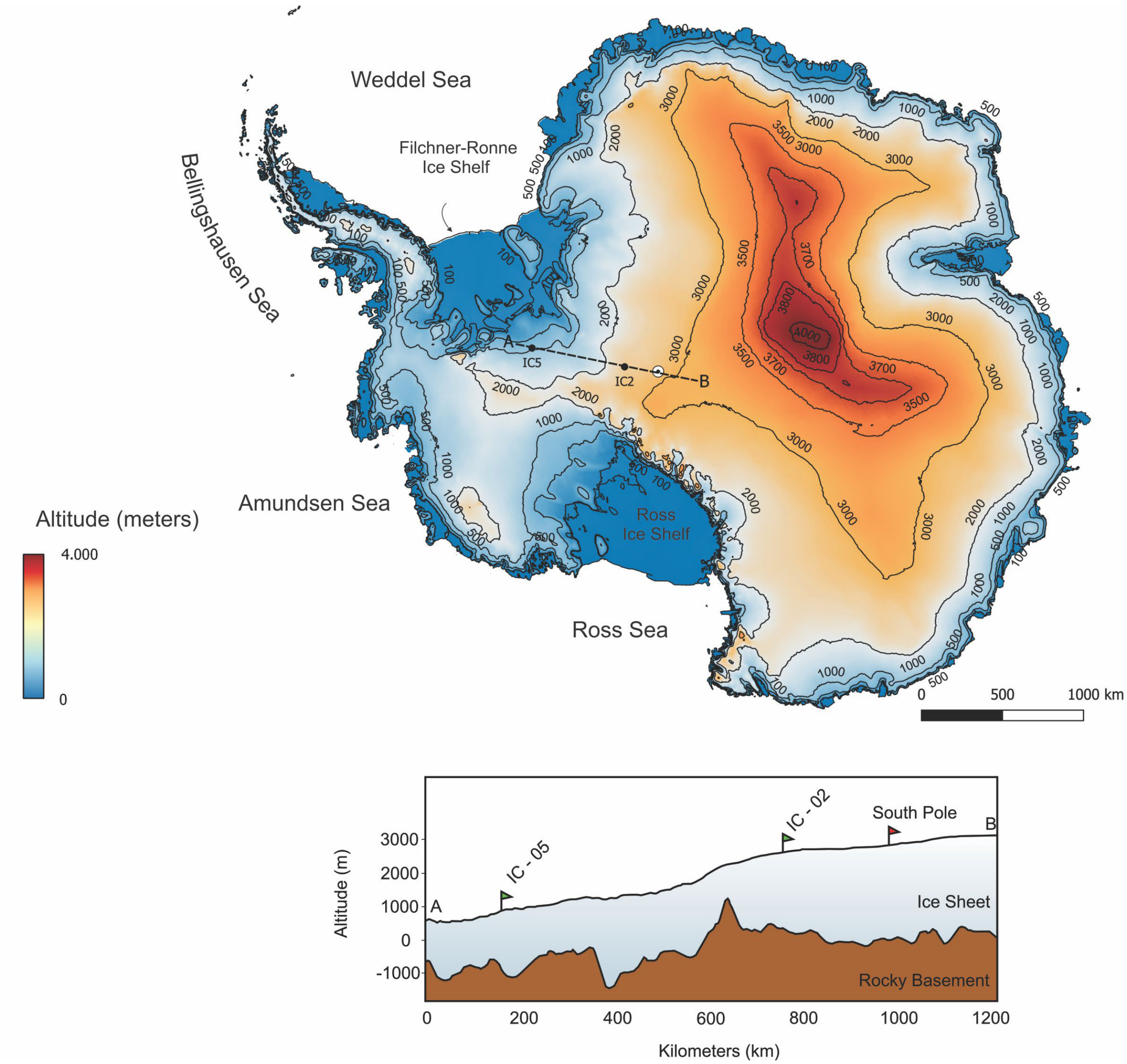

Figure 1. Antarctic ice sheet topographic map. The two firn cores (IC-02 and IC-05) sites are marked on the map and in A–B cross-section. The white dot on the map identifies the Geographic South Pole.

The two firn cores were collected approximately 220 km apart, thus having different geographic and glaciological conditions. The IC-02 was collected at the coordinates 88°01’21.3” S and 82°04’21.7” W, about 220 km from the Geographic South Pole and at an altitude of 2,621 m in typical Antarctic Plateau environmental conditions: dry, very low precipitation, and low temperatures (Owens & Zawar-Reza, 2015). In total, 42.92 m of firn were recovered in 44 sections (diameter 8.25 cm). The temperature at a depth of 10 m, measured with a calibrated silver resistance, was -45.0 ± 0.5°C.

The IC-05 was collected at the coordinates 82°30’30.8” S e 79°28’02.7” W in the WAIS, at an altitude of 950 m. In total, 42.51 m of firn were recovered in 44 sections. The temperature at a depth of 10 m was -29.0 ± 0.5°C. This core is in a site closer to the coast, at a lower altitude and with a higher annual precipitation rate than the IC-02 site.

After the end of the traverse, all boxes containing the firn cores were transported by air to Punta Arenas, Magallanes y Antárctica Chilena (Chile) and from there to the New York airport, in cold storage and always below -15°C. From the last location, they were transported by refrigerated truck to Bangor, Maine (USA), where they were stored in commercial cold storage chambers at -20°C, until subsampling at the Climate Change Institute (CCI).

The IC-02 core was previously analyzed by Gerhard (2019) and Tavares (2020), who produced the ion chromatography and stable isotope data. The upper part of the IC-05 was partially studied by Da Silva (2011) for ionic concentration. This article presents new ion chromatography and stable isotopic (δD) data for the IC-05 and compares with the existing data for the IC-02.

Decontamination and sub-sampling

The decontamination and sampling process took place at the CCI and rigorously followed the procedure presented by Osterberg et al. (2006) for both firn cores. In a cold room class 100 (ISO 14644-1:1999) with a temperature of -20 °C, the firn cores had their bases, tops, and sides scraped with a ceramic knife, previously cleaned with methanol, to remove any parts that touched the drill parts. About 2 to 4 mm of firn core were removed in a table, also previously cleaned with methanol and under laminar horizontal air flux, and then stored in acrylic tubes. After decontamination, the firn cores sections were submitted to a continuous melting and discrete sampling process, sorting out aliquots for trace elements analysis by mass spectrometry with inductively coupled plasm (ICP-MS), ion content analysis, and stable isotope analysis. The continuous melting with discrete sampling (CMDS) was made with the firn core inside a vertical freezer and positioned above a 3 mm thick nickel plate (> 99.99% Ni) that itself is above an aluminum base warmed up between 15 and 25 °C. The nickel plate has radial grooves 200 µm wide to drain the liquid produced from the firn core melting. It also has a 1 mm high ring, which segregates the liquid coming from the central part of the firn core from the liquid that comes from the outer part of the firn core. The liquid from the central part is considered purer and therefore designated for ionic and trace element analysis. The liquid from the outer part of the firn core, on the other hand, is considered more prone to contamination, and so it is designated to stable isotope analysis. The liquid is pumped to polypropylene or high-density polyethylene vials previously sterilized with deionized water. About 25 to 50 mL of sample are stored in each vial to be forwarded to analysis. The melting flux varied between 1.5 cm min^{-1} and 3.5 cm min^{-1}. Between each melting session, the system pumps ultraclean water (MiliQ-Element > 18,2MΩ. cm). Further details of this procedure can be found in Osterberg et al. (2006). Immediately after this procedure, the samples were frozen to avoid isotopic fractionation.

Stable isotopic analysis

The stable isotope analysis was carried out following the cavity ring-down laser spectrometry technique presented by O'Keefe & Deacon (1988). For that, it was used a WS-CRDS Picarro® L2130i spectrometer located at the Laboratório de Glacioquímica from the Centro Polar e Climático (CPC) from the Universidade Federal do Rio Grande do Sul (UFRGS). The spectrometer was equipped with an auto-sampler (A03250), a vaporizer (A0211), an analyzer (L2130i), two peristaltic pumps, a sample tray, and two syringe cleaning stations. For each sample, eight analysis protocols were done, using different aliquots to reduce the error associated with the memory effect. The syringes were cleaned between each measurement using ultra-clean water and a methylpyrrolidone solution. The analysis was made from the vaporization under temperatures of 110 °C of 2 µL of samples carried to the optical cavity by pumped N_2 gas. The results are transformed to delta (δ) values compared to the international standard V-SMOW2 *per mille* (‰). The measurement precision was 0.9‰ and 0.4‰ for the δD and the $\delta^{18}O$, respectively. The following equation was used to obtain the delta notation:

$$\delta^{18}O = \left(\frac{\left(\left({}^{18}O/{}^{16}O\right)sample - \left({}^{18}O/{}^{16}O\right)VSMOW\right)}{\left({}^{18}O/{}^{16}O\right)VSMOW}\right) \times 10^3\ ‰ \tag{1}$$

Parameter calculations were utilized for the interpretation of results. The stable isotope analysis provides the parameter known as deuterium excess (*d*), defined by Dansgaard (1964), and represents the differential fractionation that the deuterium presents to the oxygen when submitted to variable evaporation rates. The difference in fractionation is compared to the global meteoric water line proposed by Craig (1961a, b) according to the following equation:

$$d = \delta D - 8(\delta^{18}O) \tag{2}$$

The difference in isotope fractionations is mainly controlled by the evaporation source area's physicochemical characteristics (Schlosser et al. 2008). Hence, the deuterium excess results provide information about the air masses source areas.

Ionic chromatography analysis

The first 200 IC-02 samples, which represent the first 7.11 m depth, were analyzed using the High-Performance Ion Chromatography (HPIC) technique, following the procedures of Weiss (2016). This part of the analysis was carried out at the CCI's laboratories, University of Maine, Orono, ME, as described by Lindau (2014). Two chemical-suppression Dionex DX-500 ionic chromatographs with conductivity detectors coupled to two samplers (passers) Gilson model 222XL Liquid Handler were used, the operation characteristics are described in the table below (Table I).

Weekly calibrations were performed in the chromatography systems using five standard stock solutions (Ultra Scientific, USA) containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}. The standard solution used for the methylsulfonic acid (MSA) was produced from a reagent made available by Fluke Analytical

Table I. Characteristics of the ionic chromatography systems of the Climate Change Institute (CCI), University of Maine, Orono, ME, USA.

Ion Chromatograph Dionex 500		
System	**Cations**	**Anions**
Injection Loop	500 µL	500 µL
Flux	1 mL min^{-1}	1 mL min^{-1}
Guard Columns	-	AG-11
Analytic Columns	CS-12A	AS-11
Suppressor	CSRS-300	ASRS-300
Detector	CD20	CD20
Eluent	MSA (25 mM Isocratic)	KOH (gradient of 1 mM to 8 mM)

(Lindau 2014). The concentration curves presented a correlation coefficient (r) greater than 0.99, and the ionic concentrations were measured with a 0.1 ppb precision (Hammes 2011). The variation in the detection signal was defined by analyzing the blank samples composed of deionized water from the laboratory and following the methodology described by EPA 300.1 (Hautman & Munch 1997). Table II below shows this variation for each ion.

The deepest 248 samples, from 7.11 m to 14.57 m depth, were analyzed at the laboratory class 7 (ISO 16499-1:1999) of the Centro Polar e Climático (CPC) at the UFRGS, Porto Alegre, RS, Brazil, following the methodology described by Thoen (2017). For these analyses, two chromatographs were used: Dionex™ ICS2000 (anions) and Dionex™ ICS-2100 (cations) with 2 mm diameters columns coupled with automatic injection for the sampler (Dionex™ AS-DV). The function characteristics for the CPC chromatographs are listed below (Table III).

The sulfate and the sodium were used to calculate the non-sea salt sulfate ($nssSO_4^{2-}$) according to the following equation (Wolff et al. 2006, Sneed et al. 2011):

$$nssSO_4^{2-} = SO_4^{2-} - ssNa^+ \left(\frac{SO_4^{2-}}{Na^+}\right)_{sea\ water} \tag{3}$$

where the seawater ratio SO_4^{2-}/Na^+ is considered 0.251 and constant.

Dating of the firn cores

Stable isotopic ratios and ionic concentration seasonal variability were used to date the two firn cores. The strong isotopic signal seasonality allows for the determination of summer peaks (i.e., greater values) and winter valleys (i.e., lower values) (Dansgaard et al. 1969, Epstein et al. 1970, Hou et al. 2013). This variation is considered an excellent proxy of the climate seasonality record in firn and shallow ice cores (Legrand & Mayewski 1997). The ion chromatography results were also used

Table II. Variation in the detected signal for the CCI's ion chromatography systems (modified from Lindau 2014).

Ion	Variation (µg L-1)
Na^+	1.29
K^+	0.29
Mg^{2+}	0.51
Ca^{2+}	0.63
Cl^-	1.78
NO_3^-	0.35
SO_4^{2-}	0.76

Table III. Characteristics of the ionic chromatography systems of the Centro Polar e Climático (CPC/UFRGS), Proto Alegre, RS, Brazil).

Ion Chromatographer Dionex – 2100/2000		
System	**Cations**	**Anions**
Injection Loop	200 µL	200 µL
Eluent Gradient	6 – 16 mMolar	13 – 40 mMolar
Eluent Flux	0.25 mL min^{-1}	0.25 mL min^{-1}
Eluent	MSA	Potassium Hydroxide
Separation Column	Ion Pac CS19 2 mm	Ion Pac AS18 2 mm
Suppressor current	6 mA	22 mA
Suppressor Type	CERS500 2mm	AERS500 2mm
Detector	CD20	CD20
Work Pressure	± 2000 PSI	± 1900 PSI
Temperature Detector	35.0 ± 0.1 °C	35.0 ± 0.1 °C
Background Detector	< 0.3 µS cm^{-1} (*typical*)	< 0.6 µS cm^{-1} (*typical*)
Run time	27 min	27 min
Data Analysis System	Chromeleon 7.2™ Software	Chromeleon 7.2™ Software

to establish a chronology for the cores. Like the Na^+ and the MSA, some ions show a well-marked seasonality. The Na^+, for example, has peaks of maximum concentration in the winter, due to a greater influence of sea spray over the Antarctic continent, whereas the MSA^- has its maximum concentration in the summer, when the increasing marine biologic activity after sea ice melts produces organic compounds that react with atmospheric gases to form the MSA that is later deposited within aerosols in the Antarctic ice sheet (Legrand & Delmas 1984, Legrand & Mayewski 1997, Curran et al. 2003, Cuffey & Paterson 2010). The peaks and valleys were identified and counted visually using 2004/2005 austral summer as a starting point when the drilling was performed. Another essential proxy that assisted the dating process was the non-sea salt sulfate ($nssSO_4^{2-}$) concentration, a volcanic marker. For example, in 1992, the $nssSO_4^{2-}$ had a significant concentration peak probably associated with the Pinatubo and Cerro Hudson's eruptions.

The density variation along the firn cores allowed to transform the depth in meters to meters of water equivalent (m w.eq.) allowing to derive the net annual accumulation time series for each core.

Air mass trajectories and air surface temperature

The backcasting model called Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) was used to determine air masses trajectories clusters for the two core sites. NCEP meteorological data were used to run the models. Models of trajectories were made for two months (during summer and winter apexes, *i.e.,* February and August) for an altitude of 1000 m above ground level using UTC 10:00 and with duration time of 120 hours. The clusters were modelled for a time span of 120 hours every 6 hours for every day of the two chosen months between the years 1980 and 2000. Maps with the trajectories clusters for the chosen months were made to better assess the possible source areas. Temperature anomaly data for the region for the studied period were derived from the Climate Reanalyzer, maintained by the Climate Change Institute, University of Maine, Orono. Monthly air temperature records from the Amundsen-Scott (90°S), Belgrano II Station (77°52'25" S, 34°37'39"W) and Halley Station (75°34'05" S; 25°30'30" W), retrieved from the Met READER, were used to make comparisons with stable isotope ratios variability of the two firn cores.

RESULTS

This article analyzed the first 488 samples for the IC-02, achieving a depth of 14.58 m, and the first 602 samples for the IC-05, reaching 19.73m. The samples were analyzed for stable isotope by laser spectrometry and for ion concentration by ionic chromatography. The interval for both firn cores represents 25 years or record.

Stable Isotope

The proportion of deuterium (δD) and oxygen-18 ($\delta^{18}O$) in the IC-02 was determined for 436 and 352 samples, respectively. For IC-05, 577 samples for deuterium and 380 for oxygen-18 (Figure 2). Table IV summarizes the stable isotope ratios in the two firn cores.

In the IC-02, the mean value of δD is 380.1 ± 13.2‰, varying from 408.2‰ to 336.0‰ The IC-05 has values of δD varying from -335.5‰ to -227.4‰ with a mean value of -285.8‰ and standard deviation of 21.3‰.

Table IV. Statistics for the stable isotope data in the IC-2 and IC-5 firn cores for the 1978–2003 period.

	Stable Isotope ratios in *per mille* (‰)					
	IC-02			IC-05		
	δD	$\delta^{18}O$	d	δD	$\delta^{18}O$	d
Minimum	-408.18	-50.77	3.24	-334.11	-40.40	0.53
Maximum	-347.64	-43.71	8.73	-227.44	-30.99	6.79
Mean	-375.08	-46.80	5.38	-285.60	-35.95	3.24
Standard Deviation	13.52	1.36	1.17	21.38	2.17	1.35

Table V. Ionic concentration (in µg L-1) in the IC-02 and IC-05 for the 1978–2002 period.

Analytes (µg L^{-1})	IC-02					IC-05				
	Min	Max	Mean	Standard deviation	N° samples	Min	Max	Mean	Standard deviation	N° samples
Na^+	0.01	65.60	13.65	8.98	440	3.51	693.12	66.68	83.66	574
Mg^{2+}	0.24	25.71	2.09	1.49	444	0.77	74.80	9.35	8.90	573
SO_4^{2-}	19.37	179.80	55.34	21.45	445	13.09	730.5	58.01	56.25	572
$nssSO_4^{2-}$	17.81	173.67	51.86	21.61	439	0.26	681.74	47.09	53.85	521
Cl^-	15.89	150.63	35.11	12.25	446	15.40	1251.80	135.84	148.14	572
MS^-	1.01	25.73	8.13	6.77	436	2.68	48.46	17.98	7.79	258

The $\delta^{18}O$ in the IC-02 ranges from -49.5‰ to -35.9‰ with a mean value of -46.5 ± 2‰, and in the IC-05 ranges from -40.4‰ to -31.0‰ with mean value of -36.0 ± 2‰.

In the IC-02, the derived *d* ranges from 3.34‰ to 9.73‰, mean of 5.4 ± 1.2‰, and in the IC-05, it ranges from 0.53‰ to 6.69‰, with mean value 3.2 ± 1.4‰.

The stable isotope time series shows the well-marked seasonal behavior (Figure 2), with peaks in summer and valleys in winter. The correlation between the hydrogen and oxygen isotopic ratios is high in the two cores (r = 0.956 and 0.997, respectively in IC-02 e IC-05), maintaining Craig's line (Global meteoric water line; Craig, 1961a). The seasonality of IC-02 is better defined than that of IC-05. In contrast, other parts of the last record have plateaus formed by peaks and valleys whose differences between summer and winter are small.

Ion Chromatography

Table V shows the results for the ion chromatography analyses. Note that some ions did not have their concentrations determined in some samples due to technical problems. The ionic concentration profiles for the two cores are shown in Figure 3.

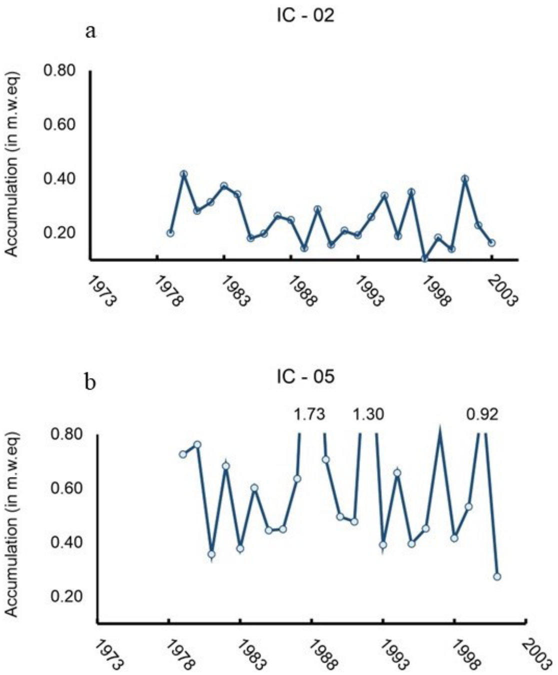

Figure 2. Accumulation time series (m.w.eq.) at the IC-02 (a) and IC-05 (b) firn cores sites.

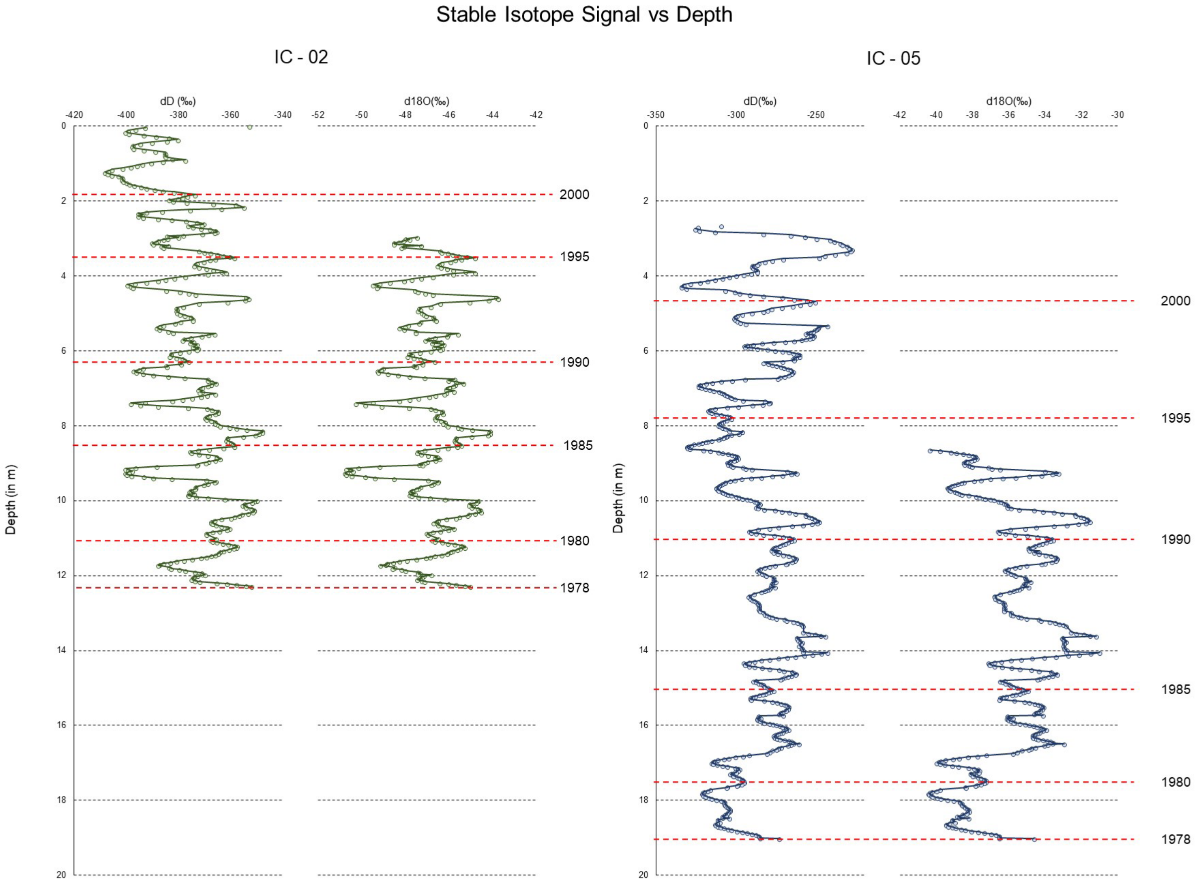

Figure 3. Stable isotope ratios time series (in ‰ relative to the international standard V-SMOW2) for the firn cores IC-02 and IC-05.

Accumulation

The annual net accumulation, inferred from the stable isotope seasonal variation after correcting the sample density, varies from 0.11 m w.eq. to 0.42 m w.eq. at the IC02, with an annual mean of 0.25 ± 0.08 m w.eq. At the IC-05 location, the accumulation varies from 0.19 m w.eq. to 0.98 m w.eq., with an annual mean of 0.35 ± 0.32m w.eq. (Figure 4). The statistics are shown in Table VI.

Air masses trajectories for the months of February (summer, SM) and August (winter, WM) between the years of 1980 and 2000 (Figure 5) were modelled and then clusters of frequency were calculated. These two months were chosen due to their representativity of the summer and winter seasons. During the SM, the firn cores sites presented different source areas for air masses. The IC-02 which is closer to the South Pole has as its main source of air masses the Antarctic Plateau, especially the region of the Dome Fuji (Figure 5a). The IC-05, differently, has more diversity of air masses sources. The main source is the Coats Land but there are also air masses coming from the WAIS, mainly from the Transantarctic mountains and the Marie Byrd Land but also from the Amundsen and Bellinghausen seas (Figure 5b). During the WM, there seems to be a diversification of air masses influencing the IC-02 site. Its main source region is the Dronning Maud Land and the Brunt Iceshelf but there is also influence coming from the Pensacola mountains and the Amundsen Sea. The influence of higher terrain, such as the Domi Fuji is weaker (Figure 5c). The IC-05, on the other hand, is mainly influenced

Table VI. Annual accumulation data (in m w.eq.).

	Annual accumulation (m w.eq.)	
	IC-02	**IC-05**
Minimum	0.11	0.19
Maximum	0.42	0.98
Annual average	0.25	0.35
Average 12 m depth temperature	-45.0 ± 0.5°C	-29.0 ± 0.5°C

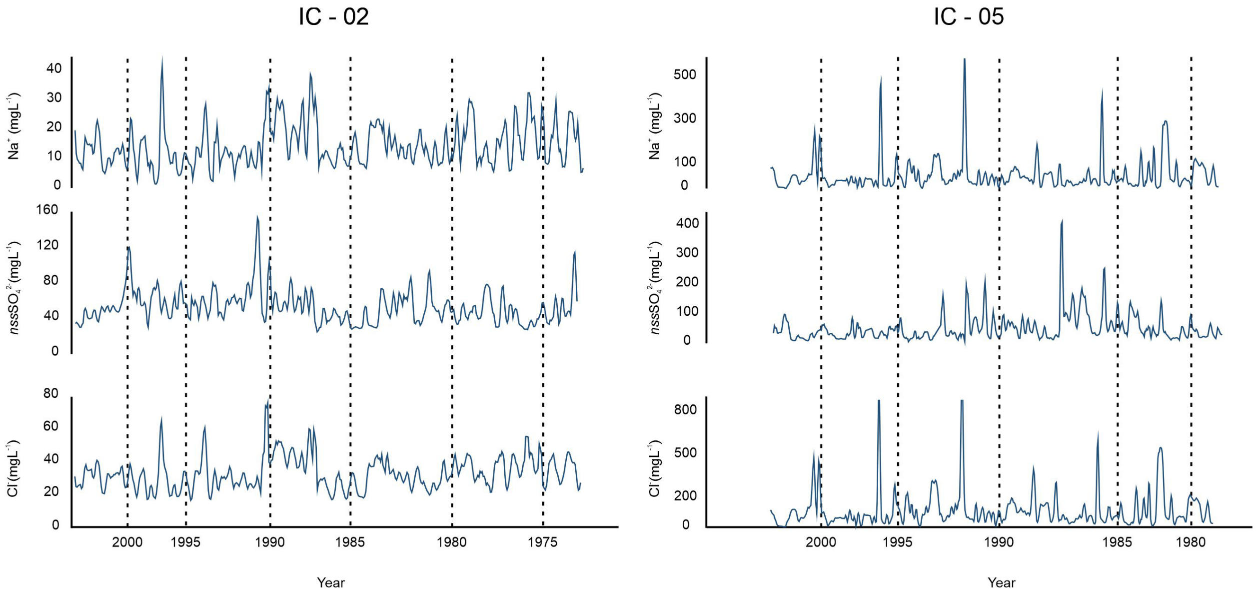

Figure 4. Time series for the concentrations of the analytes measured by ion chromatography (in μg L^{-1}) in the IC-2 e IC-5 firn cores. Air Masses Trajectories.

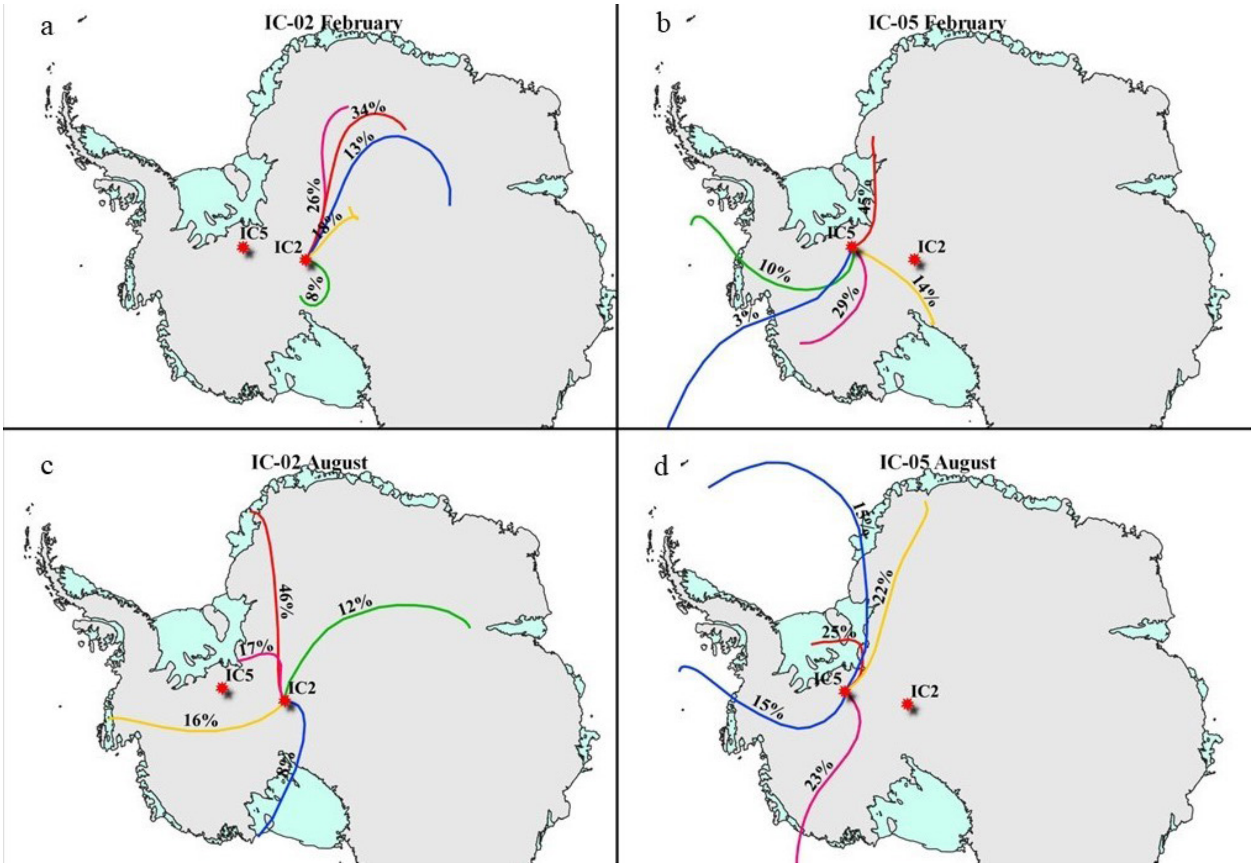

Figure 5. Air masses trajectories clusters for the firn cores sites IC-02 and IC-05. Summer month (February) for the IC-02 (a) and for the IC-05 (b). The winter month (August) for the IC-02 (c) and the IC-05 (d).

by air masses coming from the WAIS region, with Filchner-Ronne ice shelf playing an important role during WM. Secondary sources are the Ross Sea and the Marie Byrd land. There is minor influence of the Dronning Maud land, the Weddel Sea and the Bellingshausen Sea (Figure 5d).

DISCUSSION

Air Masses

The results shown by the HYSPLIT cluster analysis indicate a clear importance of katabatic winds at the IC-02 site during SM with 91% of the calculated trajectories coming from the Antarctic Plateau, while the remaining derive from the Transantarctic mountains, mainly from the Queen Maud Mountain region. During WM, the katabatic winds are less influent, and a major coastal influence seems to be affecting the site. At the IC-05, on the other hand, there seem to be no katabatic wind influence coming from the Antarctic Plateau, although there might exist some influence of katabatic winds coming from the nearby mountains, and the greater influence is clearly coastal air masses.

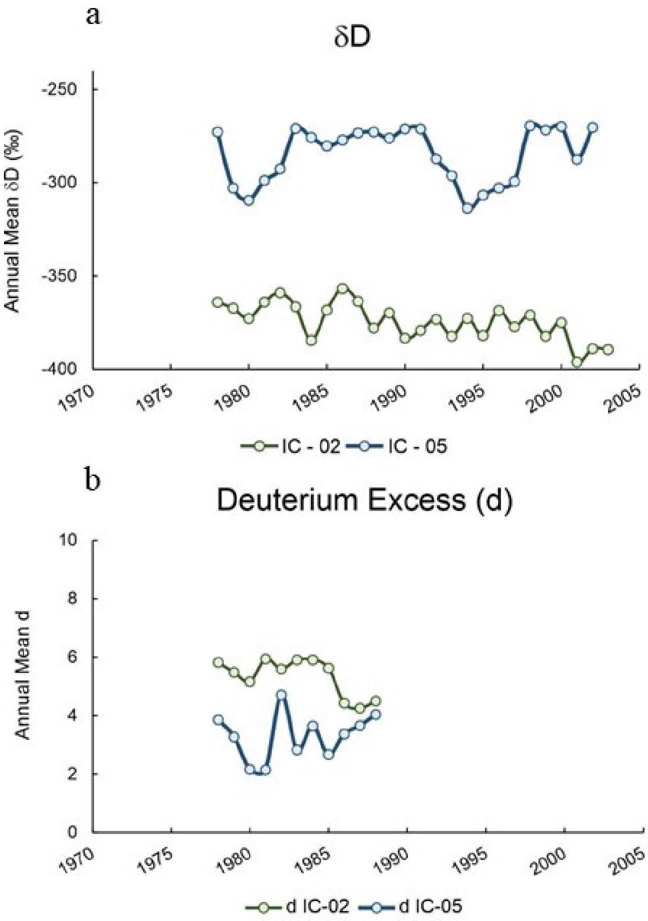

Figure 6. The annual δD (a) and the d (deuterium excess) (b) time series in the IC-02 and IC-05 firn cores.

Stable Isotope

The two isotopic ratios are about 1.3 times more negative in the IC-02 core than in IC-05 one (Figure 6). These differences are coherent since it reflects stronger fractionation processes as latitude and altitude progressively increase from the IC-05 to the IC-02 site.

There is no statistically significant correlation between the stable isotopic ratios of the two firn cores and monthly air temperature at the nearest meteorological station, the US Amundsen-Scott station ($r^2 = 0.06$, $p < 0.05$) at the South Pole in the case of IC-02, and the British Halley station (75°35' S, 26°40' W, on the Brunt Ice Shelf, $r^2 = 0.05$, $p < 0.05$) and the Belgrano II station (77°52'25"S, 34°37'39"W, $r^2 = 0.07$, $p < 0.05$) in the case of IC-05. Hence, the local temperature is not affecting immediately the stable isotope composition, although it may affect over a longer period of time. The stable isotope composition is, therefore, mainly influenced by other factors, such as the geographical conditions, air masses trajectories and physicochemical conditions of the source areas.

There is a statistically significant difference in mean deuterium excess values between the two firn cores, which is confirmed by the ANOVA analysis (F critical = 4.16; F = 66.53, $\alpha = 0.05$). The core closer to the coast (IC-05) presents lower values (Figure 7). This is expected, as the d is positively correlated with the isotopic fractionation process. That is, the more fractionated the water vapor is, the higher are the deuterium excess values. Therefore, sites in the center of the Antarctic Ice Sheet will have the highest deuterium excess values, as previously stated by Hou et al. (2013).

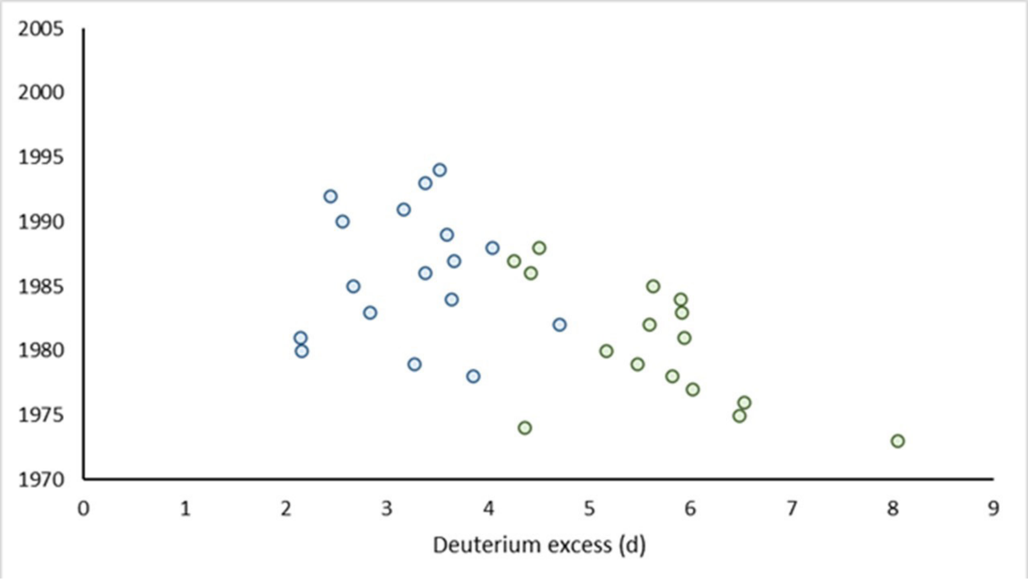

Figure 7. **Variation in d values in both sites versus time.**

Furthermore, the distance of the moisture source is also important, so longer air masses trajectories will result in a stronger fractionation process and higher d. The results obtained via HYSPLIT present variable air masses sources for both sites as discussed before, with the exception of February for the IC-02 in which most of the air masses sources are derived from the Antarctic Plateau, near the Dome Fuji area. However, it is not possible at this moment to establish any correlation between higher d values and longer trajectories for the given sites. Other factors seem to be more influent in this case, such as physicochemical conditions during the fractionation process (evaporation rate and sea temperature at source area), air relative humidity and wind speed as noted by Jouzel & Merlivat (1984) and Ciais et al. (1995). Bréant et al. (2019) showed the importance of summer katabatic winds in the deuterium excess. The IC-02 deuterium excess might have higher values also due to its strong influence by katabatic winds coming from the Antarctic Plateau, which is not the case at the IC-05.

Ion Chromatography

The chromatographic time series points out differences between the two firn cores. Both Na^+ and Cl^- have higher concentrations in the core near the coast (IC-05). The mean Na^+ concentration in this core is five times greater than in IC-02 (Na^+ 13.31 µg L^{-1}) and even ten times greater in some years. The chloride ion followed a similar pattern, with concentrations about three times greater than the mean annual IC-02 concentrations. In 1982, the Cl^- was eight times more concentrated than the IC-02. The annual mean Cl^-/Na^+ ratio for the IC-02 is 2.77, while the IC-05 is 1.99. According to Warneck (1999), the Cl^-/Na^+ ratio for sea salt is approximately 1.79. So, the IC-05 presents a Cl^-/Na^+ ratio very similar to the sea salts, while the IC-02 has a ratio that reflects the excess of the chloride ion in relation to the sodium, which is mainly derived from the sea salt (Figure 8). The results are in accordance with the data from Legrand & Mayewski (1997) that affirm that coastal sites present few or no excess of Cl^-, while areas in the center of Antarctica present excess in Cl^-. The excess of Cl^- in regions located in the Antarctic interiors are explained by the influence of atmospheric acids, like the HCl^-. Furthermore, volcanic eruptions may contribute to the entry of more HCl^- (Legrand & Mayewski 1997). There is a peak for the Cl^-/Na^+ ratio in 1998 for the IC-02. No known large volcanism that could influence such

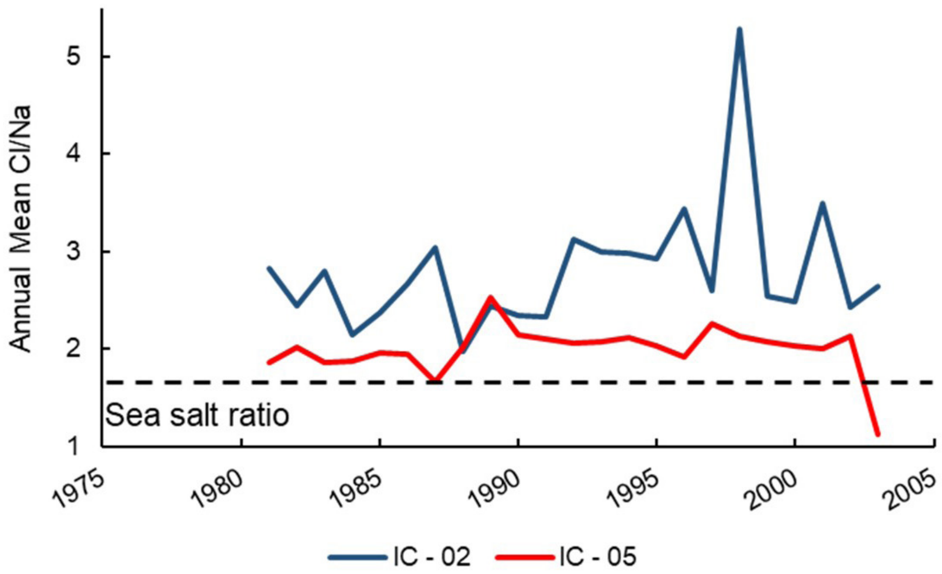

Figure 8. **Comparison of time series for Cl^-/Na^+ in both firn cores. The black dashed line indicates the typical sea salt Cl^-/Na^+ ratio.**

a remote site occurred during this time. The analysis of trajectories for this particular year revealed that most air masses came from coastal regions, mainly the Coats land (54%) and the Dronning Maud (17%) land with minor influence (up to 13%) coming from the Marie Byrd land and the Bellingshausen Sea. Pasteris et al. (2014) has suggested that peaks in chloride excess could be indicative of sea ice extent, with positive correlation and that this excess would be the result of fractionation of the sea salt. Hanna (2001) correlated an anomalously high sea ice peak in 1998 due to an exceptionally strong El Niño Southern Oscillation in the same year. The 1998's chloride peak in this study could indicate that such events had influence in the IC-02 site, near the South Pole.

The time series of $nssSO_4^{2-}$ and Cl^- show concentration peaks in 1991 in the IC-02 site (Figure 4). According to Cole-Dai & Mosley-Thompson (1999), the Pinatubo (Philippines) eruption of April 2, 1991, had a VEI (Volcanic Explosivity Index) of 6 (Global Volcanism Program, 2013). This was followed by the Cerro Hudson (Chile) eruption of August 8, 1991, with VEI 5 (Global Volcanism Program, 2013). The two eruptions signals are widely known and detected in Antarctica. However, they seem not to be the main reason for these peaks because of the 2-years delay in the glaciochemical signal response due to residence time of aerosols in atmosphere (it would be expected to find such signals during 1993 to 1994, not 1991) and because the chloride signal does not represent an excess, that is, it is followed by the sodium concentration, indicating that this might be a sea salt signal. Nevertheless, there is a peak for $nssSO_4^{2-}$ observed in the IC-05 in 1987. One possible source for the increase might be the Galunggungg (Indonesia) eruption (which started in April 1982 and had VEI 4, Global Volcanism Program, 2013), but further evidence is needed to confirm this influence.

Accumulation

The accumulation data here presented generally agrees with other studies, a reduced annual net accumulation rate in the Antarctic plateau (IC-02) than in a site nearer to the coast and at a lower altitude (IC-05). Although only 220 km apart, the IC-02 mean annual accumulation (0.23 m w.eq.a^{-1}) is more than twice the precipitation at the Geographic South Pole (0.0845 ± 0.0084 m w.eq.a^{-1}, Mosley-Thompson et al. 1999). The results also agree with precipitation values estimated by the Regional Atmospheric Climate Model (RACMO 2), assessed by Van Wessem et al. (2014) with a 35 km resolution. Tavares (2020) and Gerhard (2019) calculated the annual accumulation for the IC-02 using 85 years of data. These authors obtained a result of 0.152 ± 0.064 m w.eq. a^{-1}. Comparing the accumulation rate determined from this study for the IC-02 (0.25 m w.eq. a^{-1}), whose time interval is 25 years, with the result obtained by Gerhard (2019) and Tavares (2020), it is clear that the accumulation rate has increased along the 20th century.

CONCLUSIONS

The environmental proxies derived from the two firn cores clearly show the influence of the geographical locations. A significant contribution of humid and oceanic air masses, as demonstrated by air masses sources modeling, collaborates to a greater absolute concentration of ions, mainly sea salt-related ions (e.g., Na^+ and Cl^-) in the site IC-05. At the IC-02, on the other hand, the absolute concentration of ions is smaller, although the composition is also mostly derived from sea salt. The chloride excess found was related to the sea ice extent and fractionation process of aerosols during transport. This site showed a strong influence of katabatic winds coming from the Antarctic Plateau during summer. These geographical differences also influence the stable isotope content, indicating lower fractionation at the IC-05 than at the IC-02. The higher deuterium excess at the IC-02 than at the IC-05 might be a consequence of the transport by katabatic winds to the core site, i.e. influence of the Antarctic Plateau over the stable isotope composition in the South Pole region. The snow deposited under the IC-02 environmental conditions is very different chemically and more prone to fractionation than the snow deposited under the warmer and lower altitude conditions of the WAIS (i.e., in the IC-05 site).

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