

Drilling, processing and first results for Mount Johns ice core in West Antarctica Ice Sheet

Perfuração, processamento e primeiros resultados de um testemunho do manto de gelo da Antártica Ocidental

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ABSTRACT: An ice core, 92.26 m in length, was collected near the ice divide of the West Antarctica ice sheet during the 2008/2009 austral summer. This paper described the fieldwork at the Mount Johns site (79°55'S; 94°23'W) and presented the first results of the upper 45.00 m record covering approximately 125 years (1883 – 2008), dated by annual layer counting and volcanic reference horizons. Trace element concentrations in 2,137 samples were determined using inductively coupled plasma mass spectrometry. The concentrations obtained for Al, Ba, Ca, Fe, K, Mg, Mn, Na, Sr and Ti are controlled by climate variations, the transport distance, and the natural sources of these aerosols. Natural dust contributions, mainly derived from the arid areas of Patagonia and Australia, are important sources for aluminum, barium, iron, manganese and titanium. Marine aerosols from sea ice and transported by air masses are important sources of sodium and magnesium. Calcium, potassium and strontium showed considerable inputs of both continental dust and marine aerosols.

KEYWORDS: Trace elements; Ice core; West Antarctica ice sheet; ICP-SFMS.

RESUMO: Um testemunho de neve de 92,26 m foi coletado em um dos divisores da bacia de drenagem glacial do manto de gelo da Antártica Ocidental no verão austral de 2008/2009. Este artigo descreveu os trabalhos de campo no sítio Mount Johns (79°55'S; 94°23'W) e apresentou os resultados das análises dos 45,00 m do registro superiores do testemunho e que representam cerca de 125 anos (1883 – 2008) de precipitação de neve, datados por meio da contagem anual das camadas e dos horizontes vulcânicos de referência. Os elementos-traço estudados neste trabalho foram determinados usando espectrometria de massas por plasma indutivamente acoplado em 2.137 amostras. As concentrações obtidas para Al, Ba, Ca, Fe, K, Mg, Mn, Na, Sr e Ti são controladas pelas variações climáticas, pela distância de transporte e pelas fontes naturais desses aerossóis. Contribuições naturais de poeira, oriundas principalmente das áreas áridas da Patagônia e da Austrália, são importantes fontes para alumínio, bário, ferro, manganês e titânio. Os aerossóis marinhos, provenientes do gelo marinho e transportados pelas massas de ar, são fontes importantes de sódio e magnésio. Cálcio, potássio e estrôncio apresentam aportes consideráveis tanto de poeira continental como de aerossóis marinhos.

PALAVRAS-CHAVE: Elementos-traço; Testemunho de gelo; Manto de gelo antártico; ICP-SFMS.

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INTRODUCTION

Air temperature on the surface of the Antarctic Peninsula and West Antarctica have increased dramatically in recent decades with some reports suggesting that these are the regions which are warming faster on Earth (Turner *et al.* 2006, Bromwich *et al.* 2013). Even though climate models suggest large natural climate variability over West Antarctica (Hawkins & Sutton 2012), instrumental records in this part of the continent are scarce, and there is a lack of long-term records, which make difficult the assessment on a larger time scale.

Weather information obtained from ice cores in Antarctica provide a longer and detailed historical record than the currently available from instrumental observations. The high resolution of ice records provide information about the composition of the atmosphere in the past, in particular, changes in regions of aerosols origin and transport pathways (Legrand & Mayewski 1997, Schneider *et al.* 2006, Mayewski *et al.* 2009). However, most of these records are sites in East Antarctica. Often, climate reconstructions from West Antarctica are discarded for producing inconsistent results due to discontinuous records and the lack of data (Monaghan *et al.* 2008, Steig *et al.* 2009).

West Antarctica has lower elevation compared to East Antarctica, making West Antarctica more subject to the influence of marine air masses (Noone & Simmonds 2004, Nicolas & Bromwich 2011). Places with such influence are important because they reflect more directly the atmospheric conditions resulting from changes in ocean circulation and sea ice extent.

In this study, we presented field data and the first laboratory results of an ice core obtained in West Antarctica, around 75 km from Mount Johns nunatak¹ (79°33'S, 91°14'W). The core is part of the ITASE (International Trans-Antarctic Scientific Expedition) collection, an international initiative that has the emphasis to collect data from the past 200 years (although some records reach 1,000 years) by ice cores spaced 200 km (Mayewski & Goodwin 1997).

MATERIALS AND METHODS

Drilling site

The drilling mission in the austral summer 2008/2009 was developed from a base camp near the airstrip at Patriot Hills (80°18'S, 81°22'W) in the Ellsworth mountains, as part of the multidisciplinary expedition called "Deserto de Cristal". From that point, four researchers flew by a twin-engine plane,

Twin-Otter, to the drilling site at 79°55'28 "S, 94°23'18 "W, 2,100 m of altitude, here called Mount Johns (MJ), where the ice thickness exceeds 2,400 m (project data BedMap 2: Bed Topography of the Antarctic; Fretwell *et al.* 2013).

This drilling site (Fig. 1) was selected considering the following characteristics:

1. it has a relatively high accumulation rate,
2. it is located on a drainage basin divide (separating the Pine Island Glacier drainage basin from the one that flows to the Filchner-Ronne Ice Shelf),
3. it is located in an area of air mass confluence (air masses from the Weddell, Amundsen and Bellingshausen seas), and
4. no ice cores have been drilled nearby.

Fieldwork

Drilling

Drilling was performed with the use of an electromechanical drill FELICS (Fast Electromechanical Lightweight Ice Coring System) that retrieve cores of 8.5 cm in diameter and up to 80 cm long, reaching a maximum of 160 m in depth in the ice (Ginot *et al.* 2002). The ice core MJ reached a depth of 92.26 m.

Density

Each core obtained was immediately weighed with an electronic balance, Bioprecisa BS3000A model, with a precision of 0.1 g. From this measure and the linear dimensions (length and diameter), we made the density profile by the depth (Fig. 2). Determination of density allows correcting the profile in equivalent water and then calculating the annual accumulation. MJ ice core represents 62.70 m of water equivalent after correction for density. This depth is the sum of the length of each section multiplied by its density.

MJ ice core has an average density of 0.70 g cm⁻³, ranging of 0.34 to 0.91 g cm⁻³. The density increases gradually (as expected at a site without evidence of surface melting of snow) and reaches the transition firn/ice (density 0.83 g cm⁻³) at depth 68.88 m (44.00 m in water equivalent).

Stratigraphy

The transformation of snow to ice occurs for densification (with partial air expulsion) and recrystallization. Note that in polar glaciers this whole process occurs without formation of seasonal melt water. The classification used by glaciologists (e.g., Cuffey & Paterson 2010) has the following sequence with increasing depth:

¹A rock, often the top of a mountain, surrounded by a glacier, ice cap, or mantle of ice (Simões 2004).

1. snow is usually restricted to material that has not changed much since it deposition;
2. firn are the crystals in an intermediate phase, indicating a continuous transformation of the physical properties of snow, increasing the diameter of the crystals and partial expulsion of air, while maintaining the permeability and communication with the atmosphere;
3. ice is snow that suffered intense compaction and metamorphism, whose pores are finally closed (i.e., loss of permeability), which occurs approximately when snow reaches a density of 0.83 g cm^{-3} .

MJ stratigraphy was described visually using the criteria above and density measurements (Fig. 2). First 4 m are constituted principally of fresh snow and snow with smaller grains alternating with larger grain ($> 3 \text{ mm}$) followed by firn layers until a depth of 68.80 m. The following meters until the depth of 92.26 m constitute a transition zone, alternating

layers of firn and ice. Throughout the MJ ice core, it is possible to observe millimeter ice layers. Depth hoar² layers are observed on some levels, for example the 18 m depth.

The recorded observations do not show evidence of percolation of water or refreezing across the profile. In addition, layers containing microparticles have not been observed (e.g., volcanic ash), which could be correlated to specific volcanic events.

Borehole temperature

The temperature distribution in glaciers and ice sheets depends on several factors, e.g. geothermal heat flux and heat generated by frictional heating basal slip warm or melt the base (Cuffey & Patterson 2010). However, in the first 10 to 15 m, the temperature of the snowpack is controlled by seasonal variations in air temperature. Thus, in glaciers not subjected to seasonal snow melting at the surface (the melting water would

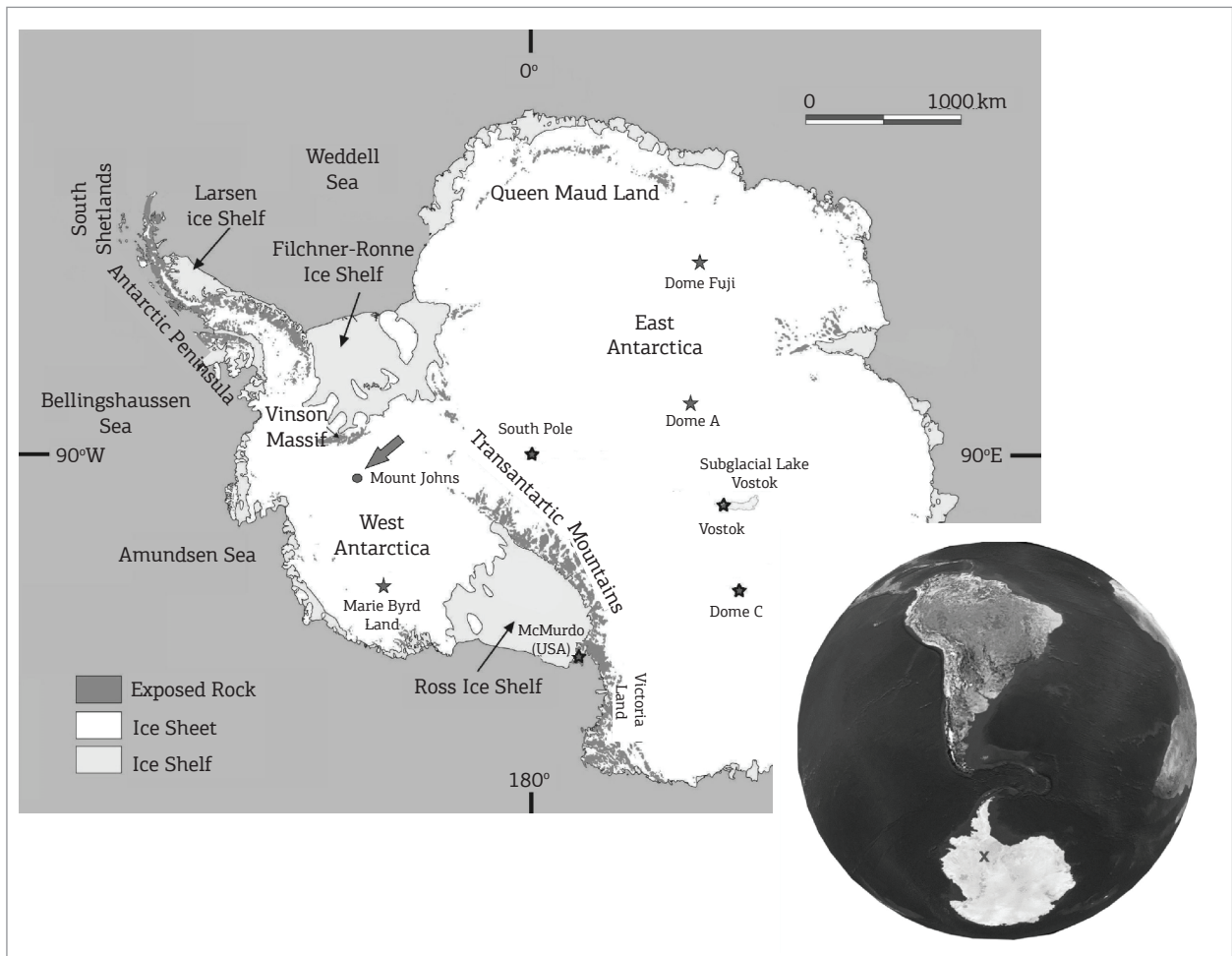


Figure 1. Map of Antarctica showing the collection site in Mount Johns ($79^{\circ}55'28''\text{S}$, $94^{\circ}23'18''\text{W}$, arrow) and the main toponyms mentioned in this paper (Figure adapted from Simões 2011). The perspective view in the lower right corner shows the Mount Johns (marked area) in relation to the southern hemisphere.

²Ice crystals larger than 3.00 mm formed between snow layers with great temperature difference (Simões 2004).

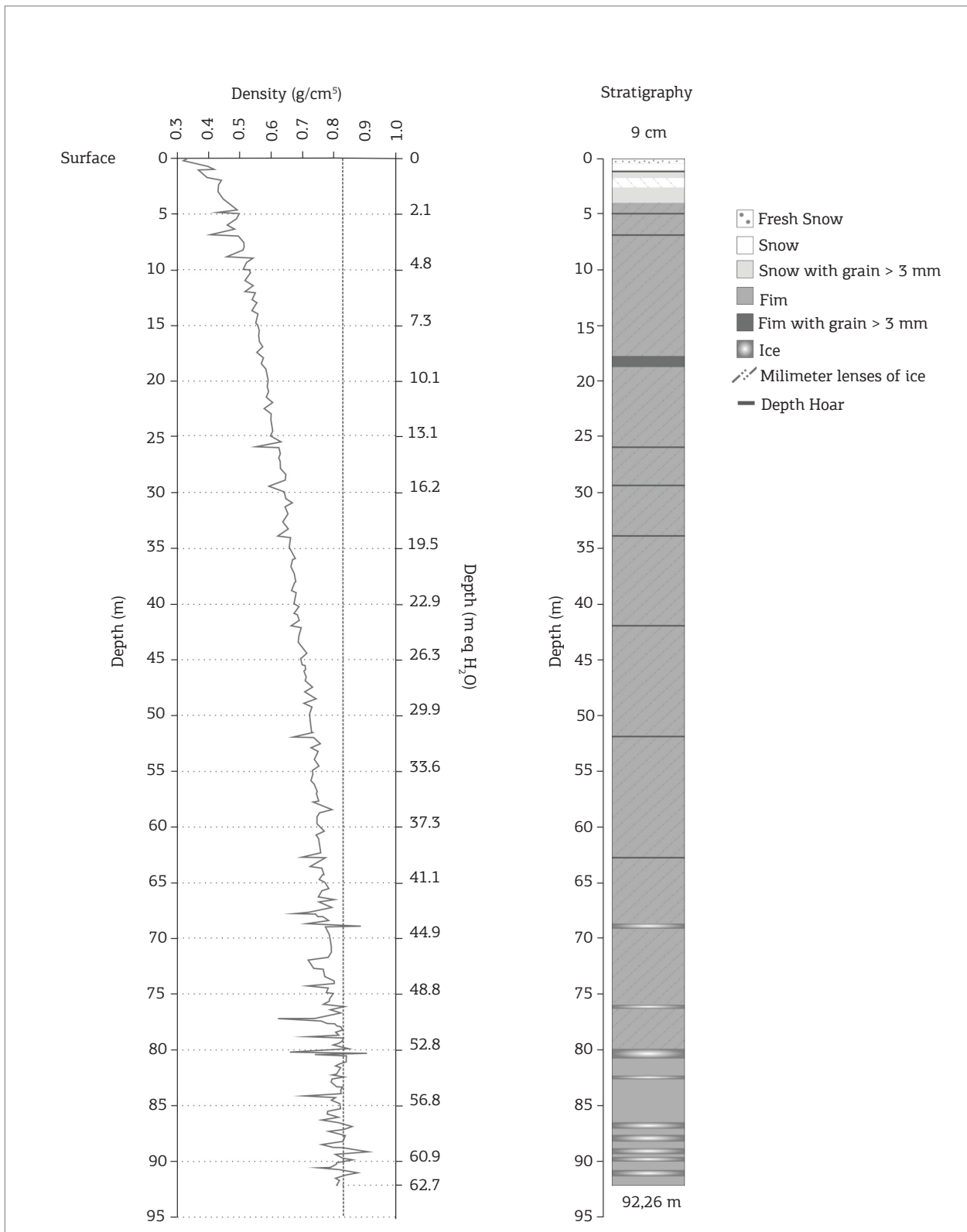


Figure 2. On the left, Mount Johns ice core density profile (in g cm^{-3}). Note the two depth scales (real depth on the left side and meter water equivalent on the right side). The dashed line marks the transition between firn and ice (i.e., density greater than 0.83 g cm^{-3}). The right profile shows the stratigraphy over the 92.26 m of the Mount Johns ice core.

liberate latent heat and increase the temperature of the snow), the temperature between 10 and 15 m is the average air temperature at the site.

Temperature at 12 m deep at MJ ice core was measured by a probe composed of a silver strength previously calibrated and placed onto the tip of an electric cable. The probe remained in the pit 24 hours for establishment of thermal equilibrium with the walls of the well. The value of the temperature measured was -33°C .

Storage and transport

Sections of 1 m in length were packed in tubular coils of polyethylene, then organized in polystyrene boxes and transported by air in a cargo plane to Punta Arenas (Chile), where they were stored in cold room at -20°C . The ice cores were flown under refrigeration in 2009 of Punta Arenas to New York and after in a refrigerator truck to Bangor, Maine, where it was kept solid in an industrial refrigerator until the time of preparation for analysis.

Laboratory work

Decontamination and subsampling by Continuous Ice Core Melter System

Sample preparation and decontamination were performed at the Climate Change Institute (CCI), University of Maine, USA. During all transport and storage, the MJ ice core remained frozen at temperatures below -20°C .

Decontamination of the MJ ice core was conducted in a certified cold room (-20°C) of class 100. The outer layer of the firn and ice was scraped (between 2 and 4 mm) using a clean ceramic knife to prevent contamination (procedure performed according Tao *et al.* 2001). The ends of each section were removed because they are most susceptible to contamination.

The core was melted using a Continuous Ice Core Melter System (housed in clean room class 100) developed by CCI researchers from the model proposed by Röthlisberger *et al.* (2000), which enables a discrete sampling and automatic quartering section. According to Osterberg *et al.* (2006), this system can simultaneously and continuously sample the ice core for three different glaciochemical analyses: major elements by Ion Chromatography (IC), trace elements by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) and stable isotopes by Cavity Ring-Down Spectroscopy (CRDS). The samples were collected into acid-cleaned (Optima HNO_3) LDPE vials and acidified to 1% with double-distilled HNO_3 before analysis.

Determination of trace elements by ICP-SFMS

Trace element concentrations (Al, Ca, Fe, K, Mg, Mn, Na, Sr, and Ti) in 2,137 samples (corresponding to the upper 45 m of the MJ ice core) were determined using the

CCI Thermo Electron Element2 ICP-SFMS coupled to an ESI model SC-4 autosampler. Working conditions and measurement parameters are described in Table 1. The ICP-SFMS is calibrated daily with five standards that bracket the expected sample concentration range. Although there is no certified reference material for trace elements in polar snow and ice, the analyzed samples were certified with water reference material (SLRS-4, National Research Council Canada, Ottawa, Canada) to ensure the concentrations within the certification range, confirming the accuracy of this method (details in Osterberg *et al.* 2006).

RESULTS

Ice core dating

The MJ ice core record (upper 45 m) was dated by annual layer counting based on seasonal variations of Na and S concentrations (Fig. 3). Based on the elemental concentrations determined by ICP-MS, the annual seasonal peaks were identified and estimated, sequentially, the deposition dates (Steig *et al.* 2005). Layer dating by this type of counting is reliable in polar ice cores, as the original deposited snow sequence is preserved because melting, percolation and refreezing processes are rare in the Antarctic and Greenland ice sheets (Cuffey & Paterson 2010).

Most of the Na in Antarctic snow precipitation originates from open ocean sources. Peaks in Na concentrations in continental Antarctica occur primarily in winter/spring due to more intense atmospheric circulation and transport during this time of the year (Legrand & Mayewski 1997, Korotkikh *et al.* 2014). Sulfur deposition in the West Antarctica ice sheet reflects both marine and non-marine

Table 1. Instrumental conditions and measurement parameters for the CCI Thermo Electron Element2 ICP-SFMS instrument.

Forward power	1280 W
Coolant gas	$\sim 16 \text{ L min}^{-1}$
Auxiliary gas	$\sim 0.85 \text{ L min}^{-1}$
Sample gas	$\sim 0.8 \text{ L min}^{-1}$
Sample cone	Ni; 1.1 mm
Skimmer cone	Ni; 0.8 mm
Sample inlet	ESI ApexQ
Nebulizer	ESI PFA-ST
Resolution (m/mm)	Low: 400; medium: 4,000 and high: 10,000
Sample uptake rate	$100 \mu\text{L min}^{-1}$
Sensitivity	800,000 cps (counts per second) for $100 \text{ ng L}^{-1} \text{ }^{115}\text{In}$
Total measurement time per sample	2 min 20 s

sources, and, in some cases, volcanic contribution is very important to the levels of this element (Steig *et al.* 2005). A regular pattern was observed in the concentrations obtained from both marine as continental origin, except anomalous peaks in the concentration profile that have been identified as major explosive volcanic events around the globe.

Major historical volcanic eruptions, such as Pinatubo (1991), Agung (1963), Santa Maria (1902) and Krakatoa (1883), were identified by large sulfur concentration peaks and were used as absolute time horizons during the timescale elaboration. Based on these data, the upper 45 m of the MJ ice core cover the period from 1883 – 2008 (± 2 years) A.D.

First results on concentration of trace elements

We measured the concentrations of 10 trace elements (Al, Ba, Ca, Fe, K, Mg, Mn, Na, Sr and Ti) in 2,137 samples. These samples represent the upper 45 m of MJ ice core, totaling about 125 years of continuous record. Table 2 shows a statistical summary of the trace element concentrations measured at Mount Johns site.

Contributions from primary natural sources in each sample were estimated using the following indicators: aluminum (Al) for rock, and soil dust and sea-salt-sodium (ss-Na) for sea-salt spray. Aluminum and sodium were chosen for being the major constituent of the earth's crust (Planchon

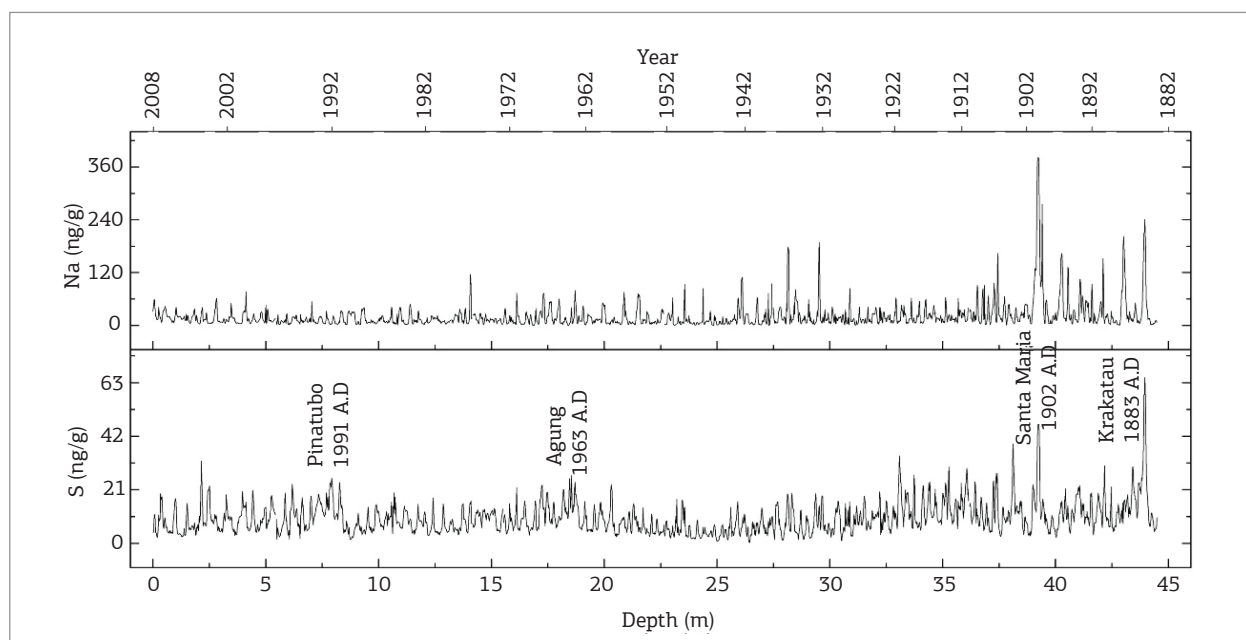


Figure 3. Mount Johns ice core timescale based on the Na and S concentration variations and major volcanic events in the period.

Table 2. Statistical summary of 10 trace elements concentration at Mount Johns ice core.

Element	Concentration			Deviation Standard (\pm)	Samples number
	Mean	Minimum	Maximum		
Al (ng g^{-1})	2.64	0.30	22.77	1.65	2132
Ba (pg g^{-1})	9.31	0.38	93.46	11.45	2120
Ca (ng g^{-1})	3.01	0.09	21.22	3.24	2095
Fe (ng g^{-1})	0.62	0.05	5.58	0.68	2124
K (ng g^{-1})	1.78	0.06	39.54	3.39	2125
Mg (ng g^{-1})	9.27	0.66	45.18	4.71	2132
Mn (pg g^{-1})	28.10	0.94	783.79	61.60	2132
Na (ng g^{-1})	21.91	0.21	381.61	33.10	2132
Sr (pg g^{-1})	23.21	0.74	117.94	17.85	2116
Ti (pg g^{-1})	14.15	0.66	209.35	18.76	2127

et al. 2002) and the main constituent of sea salt respectively (Weller *et al.* 2008, Dixon *et al.* 2013).

The soil and rock dust contribution for the trace elements studied were given by the crustal Enrichment Factor (EF_c) using the following equation (Osterberg 2007):

$$EF_c = \frac{X_{ice}/Al_{ice}}{X_{ref}/Al_{ref}}$$

in which X_{ice} is the trace element concentration in the sample, Al_{ice} is the aluminum concentration in the sample, and X_{ref} and Al_{ref} are the trace element and the aluminum concentrations in the reference material, respectively. The mean elemental concentration used for reference is the average composition of the upper continental crust taken from the literature (Wedepohl 1995).

Usually, elements with EF_c lower than 10 are considered to be non-enriched and predominantly have a crustal dust origin (Duce & Zoller 1975). Our calculations for the study period show that EF_c values for the trace elements Ba, Ca, Fe, K, Mn, Sr, and Ti are low (Tab. 3), indicating a majority terrigenous contribution to the concentration of these elements.

Marine aerosols contributions were estimated using the oceanic Enrichment Factor (EF_o) from the following equation (Osterberg 2007):

$$EF_o = \frac{X_{ice}/Na_{ice}}{X_{ref}/Na_{ref}}$$

in which X_{ice} is the trace element concentration in the sample, Na_{ice} is the Na concentration in the sample, and X_{ref} and Na_{ref} are the trace element and Na concentration in the reference material. We used the average composition of ocean water (Lide 2005) as a reference for the ocean elemental abundances.

Ca, K, Mg, and Sr presented low oceanic enrichment factor (less than 10). The results obtained show a strong marine influence in these elements. For Na and Mg marine contribution was considered the main constituent in the concentrations measured. For Ca, K and Sr both continental and marine aerosols are important sources (crustal Enrichment Factor and oceanic Enrichment Factor less than 10), details in the Table 3.

DISCUSSION

Contributions from volcanic and anthropogenic emissions were also evaluated, but, for the trace elements studied, the enrichment found these sources to be considered

insignificant. The data presented here allow a preliminary assessment of the origin of aerosol deposited at Mount Johns site, and provides a pre-classification of these trace elements.

Based on the elements analyzed, we determined that the concentrations of Al, Ba, Fe, Mn and Ti are predominantly crustal origin (dust of rock and soil), while Mg and Na concentrations have high marine influence (sea spray). Ca, K and Sr concentrations indicate influences of both sources.

Figure 4 shows a high variability of the concentrations for all studied trace elements. This variation reflects seasonality (summer and winter) and the complex process of transport and deposition. Long distances between source area and depositional site and climate interference (e.g., *El Niño*) are some of the factors affecting transport.

Marine aerosol is generated by the formation and rupture of bubbles in the open sea (Leeuw *et al.* 2011). While large particles are deposited rapidly on the ocean, smaller particles are carried along the continents, and, as a result, the amount of sea salt deposited in an interior location decreases rapidly as it moves away from the coast (Guelle *et al.* 2001).

Marine derived trace elements in inland ice cores have showed a clear seasonal signal, with highest concentrations in winter and spring (March to November), and lowest concentrations in summer (December-February) (Kaspari *et al.* 2005); the same pattern was found in our analysis (Fig. 5). Thus, marine aerosol transport in Antarctica is greater during cold periods, when sea ice extent increases the distance between the drilling site and the open sea. If the major marine aerosol source is the open sea, then a more efficient transport or a higher production rate of aerosols by bubbles bursting is required to account for the higher levels of salt spray during the winter. Previous studies have attributed high marine aerosol concentrations (in ice cores) to intensify production

Table 3. Average enrichments of elements measured in Mount Johns site for the study period. The reference element used for continental crust was aluminum (based on its high oceanic Enrichment Factor) and for marine aerosol was sodium (based on its high crustal Enrichment Factor).

Elements	EF _c	EF _o	Major influence
Al	RE	1551065	Crustal
Ba	0.44	637.39	Crustal
Ca	4.04	7.52	Crustal and marine
Fe	0.73	339308.26	Crustal
K	2.10	2.64	Crustal and marine
Mg	22.64	7.91	Marine
Mn	1.61	98351.63	Crustal
Na	31.33	RE	Marine
Sr	2.83	2.27	Crustal and marine
Ti	0.15	15258.48	Crustal

EF_o: oceanic Enrichment Factor; EF_c: crustal Enrichment Factor.

of aerosols associated with high wind speeds and turbulent conditions related to increased cyclonic activity during the winter (Curran *et al.* 1998, Kreutz *et al.* 2000).

While regional and local sources are important for sea salt aerosols, the source regions for mineral dust are located more than 4,000 km away, and, consequently, the long-distance transport, most likely through the troposphere, is decisive (Genthon 1992, Krinner & Genthon 2003). The lower elevation of West Antarctica facilitates the air masses advance (Nicolas & Bromwich 2011) and therefore it receives two to four times

more dust than East Antarctica (Neff & Bertler 2015). Studies have demonstrated that the most important source of mineral dust in this part of Antarctica are the arid and semi-arid regions of Australia, New Zealand and Patagonia (Smith *et al.* 2003, Delmonte *et al.* 2008, Albani *et al.* 2012).

The mobilization of continental dust to Antarctica reflects several factors, including climatic and environmental conditions (e.g., type and vegetation density, moisture, and soil property), so that both the land use and climate change influence on dust mobility (Prospero *et al.* 2002).

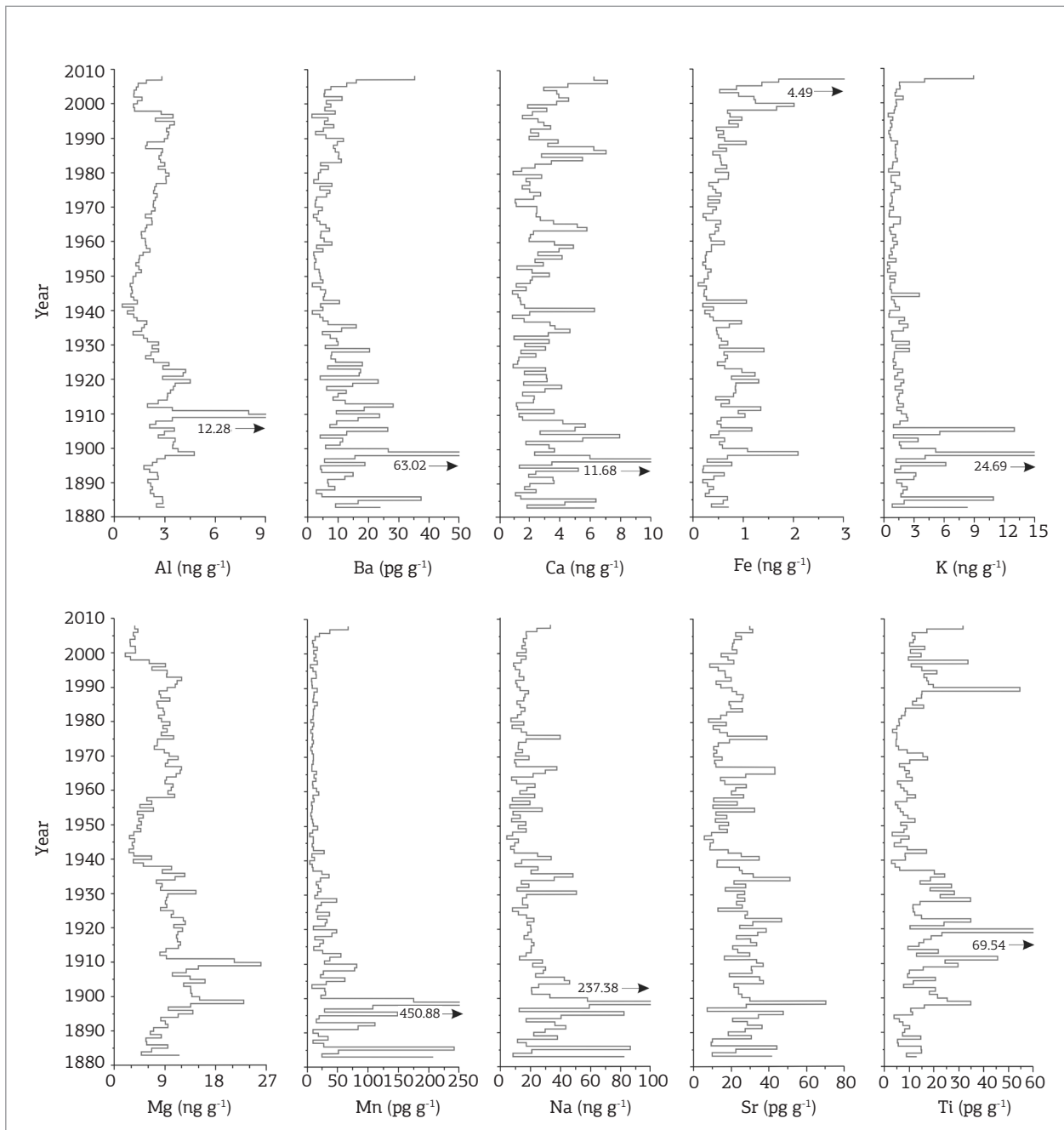


Figure 4. Profiles of Al, Ca, Fe, K, Mg, Mn, Na, Sr, and Ti measured at Mount Johns ice core, West Antarctica.

Previous studies show that deposition of dust presents a well-defined seasonal cycle (Albani *et al.* 2012), but direct observation of dust deposition in Antarctica are very difficult because of very low concentrations and variability in atmospheric deposition rates (Bigler *et al.* 2006). The first observations of the seasonal dust cycle suggested peaks in winter (Thompson 1975); later studies have questioned this evidence (Mumford & Peel 1982). Recent studies using trace elements analysis (Burn-Nunes *et al.* 2011) and atmospheric simulations (Albani *et al.* 2012) had demonstrated that the deposition of dust in East Antarctica has minimum in June, followed by maximum in late winter/spring. Observations based in aluminum concentration in the Antarctic Peninsula have indicated concentration peaks in late winter (McConnell *et al.* 2007). For West Antarctica, no data are available yet. We found in our analysis, concentrations peak in late winter/spring, consistent with deposition patterns in interior areas of East Antarctica.

Between 1883 and 2008, the high-resolution Mount Johns ice core record indicates that the trace element concentrations (mainly Al, Ba, Fe, Mg and Ti) were highly variable through time, with a declining trend in the decade of 1940 and further increase (Fig. 6). Low concentrations observed around the year 1940 would be associated with weather events; in this case, the strong *El Niño* occurred between 1939 and 1942 (Schneider

& Steig 2008), which directly affected the South Pacific and West Antarctica. Not all *El Niño* events are associated with strong anomalies in Antarctica, but some studies have shown that there is an important influence on climate variability in high latitude (Turner 2004, Bromwich & Fogt 2004).

After 1980, there is a slight increase in variability concentrations of Al, Ba, Ca, Fe, Mg and Ti, indicating that there was an increased transport of dust during this period. A study on James Ross Island (64.2°S, 57.7°W; 1600 m altitude), north of the Antarctic Peninsula, revealed that the aluminum concentration has increased substantially since 1980, coinciding with the warming of 1°C in the southern hemisphere (McConnell *et al.* 2007). This increase in dust entry into the Antarctic Peninsula is also directly related to changes in South America, especially deforestation widespread in Patagonia and northern Argentina (McConnell *et al.* 2007).

CONCLUSION

This paper presents the first results on variability of trace elements concentrations (Al, Ba, Ca, Fe, K, Mg, Mn, Na, Sr and Ti) in Mount Johns ice core between 1883 and 2008. EFC and EFO analysis suggest that the main trace elements found in polar ice are originated from various sources, such

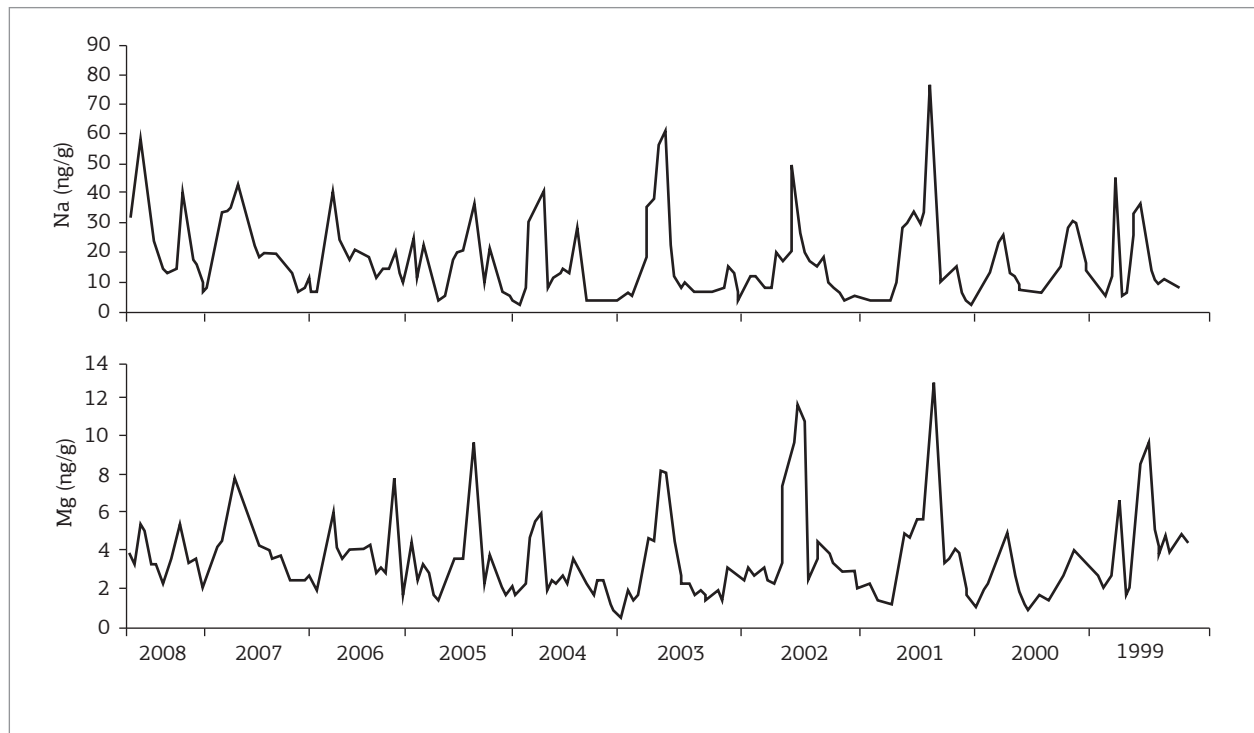


Figure 5. Na and Mg variability concentrations measured at Mount Johns ice core over a range of ten years.

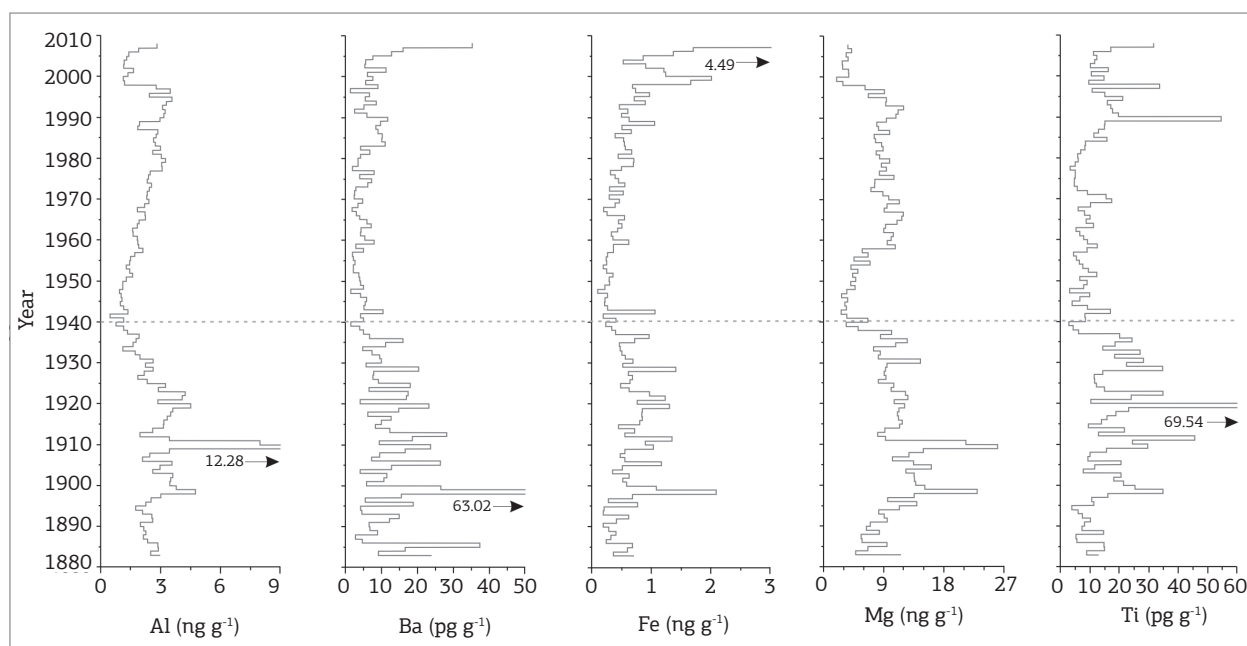


Figure 6. Mean annual concentration profile of the Al, Fe, Mg and Ti in the upper 45 m of Mount Johns ice core. Dashed line indicate a period of decrease in the deposition these trace elements.

as oceans and landmasses. Our results show a marked seasonality of mineral dust and sea spray in the trace element concentrations studied that agree with observations of previous work performed on the Antarctic Peninsula and in West Antarctica. Our results also suggest that the dust concentration at the sampling site has increased since the 1980s, a result consistent with the increase of deforestation in South America, which would generate increased availability and transport of dust to Antarctica.

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