Ice core study from the King George Island, South Shetlands, Antarctica

JEFFERSON C. SIMÕES, FRANCISCO A. FERRON, RONALDO T. BERNARDO, ALBERTO J. ARISTARAIN, MICHEL STIÉVENARD, MICHEL POURCHET, and ROBERT J. DELMAS

1Núcleo de Pesquisas Antárticas e Climáticas, Departamento de Geografia, Instituto de Geociências
2Laboratoire des Sciences du Climat et de l’Environnement – LSCE (UMR CEA/CNRS 1572)
CEA Saclay, Orme des Merisiers, 91191 – Gif-sur-Yvette, France
3Laboratorio de Estratigrafia Glaciar y Geoquimica del Agua y de la Nieve
CONICET, CC 131, 5500 – Mendoza, Argentina
4Laboratoire de Glaciologie et Géophysique de l’Environnement, CNRS, BP 96, Saint-Martin-d’Hères, France

ABSTRACT

A 49.9-m firn-ice core recovered from the King George Island ice cap (690 m above sea level) in the summer of 1995–96 was analyzed for stable isotope composition and major anionic species. Borehole temperature was measured down to a depth of 45 m, indicating an ice cap near the pressure melting point; density measurements show a firn-ice transition at a depth of 35 m. The environmental record is homogenized due to intense superficial melting, followed by percolation and refreezing. The upper 2.7 m is considered representative of the original precipitation and provides reference for the background chemical composition in the South Shetlands (δD: −72.2‰, δ18O: −9.7‰, Cl−: 120 µEq L−1, SO42−: 28 µEq L−1, excess-SO42−: 15 µEq L−1). Stable isotope seasonal variations are recognized down to 15 m, allowing dating of the core. A simple Nye’s model was used to date the core below this depth, resulting in a mean net accumulation rate of 0.59 m a−1 (water equivalent) over 73 years of precipitation. Below 37 m, the environmental record was intensively washed-out by the presence of a water table.

Key words: Glaciochemistry, ice stratigraphy, environmental record, ice cap, South Shetlands.

INTRODUCTION

Studies on variations in the stable-isotope and ionic composition of snow, firn and ice are some of the main tools in paleoclimatology, providing information on climatic conditions at different time-scales. Atmospheric circulation patterns and temperatures, relative humidity, glacial-interglacial climatic cycles and anthropogenic pollution are only some examples of information derived from ice core studies (Paterson 1994). Particularly, these studies may help to date an ice core, providing information on the mean annual rate of snow accumulation on a glacier (Dansgaard et al. 1973, Jouzel et al. 1997).

In snow and ice, which are not affected substantially by secondary processes (e.g. summer melting), the record is preserved and has been extended to 420,000 years (Petit et al. 1999). This condition is fulfilled in polar snow and ice. In contrast, investigations in subpolar and temperate glaciers are not very successful. For example, post-depositional processes such as melting, percolation and refreezing frequently obliterate the initial isotopic record.
These processes also modify the ionic content sequence by partial melting and preferential elution (Simões 1990 unpublished). This is the context over King George Island (KGI) ice cap, located under a polar oceanic climate regime (Barsch et al. 1985), where summer temperatures at sea-level are frequently above 0°C (Rakusa-Suszczewski et al. 1993, Ferron et al. 2004, this issue).

An exploratory 16 m core, drilled in the summer of 1993/94 by JC Simões near the ice core site of this work, showed a mean net accumulation rate of about 0.80 m a⁻¹ (Simões et al. 1995). On the other hand, Wen et al. (1998) recorded 2.48 m a⁻¹ for this variable. These different values are caused by the difficulties to identify annual layers based on stratigraphic or chemical information altered by the post-depositional processes. Published works on the chemical composition of snow and ice cores in KGI (e.g. Wen et al. 1998, Han et al. 1993, 1998, Han and Yoon 1990, Yan 1997), generally did not differentiate the upper non-altered layer from the rest of the core. Furthermore, some of these studies (Wen et al. 1994) were carried out at low altitudes (i.e. less than 400 m above sea level – a.s.l.) where intense superficial melting destroyed the original stratigraphical and chemical sequence of the upper layers.

In this work we interpreted the stable-isotope (oxygen and hydrogen) and anionic (Cl⁻, SO₄²⁻, NO₃⁻) variations in a 49.9 m firn and ice core (Lange Glacier ice core – Lange IC), recovered from the top of KGI in the summer of 1995/96 (Figure 1), to provide a reference for the background chemical composition in the South Shetlands and to recalculate the mean net accumulation rate at the site. Three shallow (about 5.5 m) snow-firn cores were also drilled to check the spatial reproducibility and distribution of the stable-isotope ratios (Figure 1).

SAMPLING AND LABORATORY METHODS

FIELDWORK

In the austral summer of 1995/96, a trench 1.2 m deep was dug at the top of Bellingshausen Dome (62°07’S, 58°37’W, altitude 690 m, Figure 1), at the flat ice-divide of Lange Glacier, for an ice core drilling operation. Part of the trench was used to assemble a portable (sledge transported) electromechanical drill from Laboratoire de Glaciologie et Géophysique de l’Environnement – LGGE (Figure 2), a transmitted-light table for stratigraphical description and a balance for density measurements. After the stratigraphic description, each 1 – m core section was cut in pieces of about 10 cm in length, weighed in on electronic balance (accuracy of ±0.1 g) and measured to calculate density. A sample frequency of 10 samples per meter was chosen, bearing in mind that there is an estimated mean annual net accumulation from 40 to 70 cm. This would allow for the study of seasonal changes (i.e. there was no danger of aliasing). The external parts of 423 samples were removed and stored in polyethylene plastic bags for stable isotopic analysis. The remaining part of the section was then transferred to an adjacent clean side of the trench and, under a portable laminar flow bench; all samples were decontaminated using a high-purity surgical steel saw (Figure 3). Finally, each remaining core part was stored in polyethylene plastic bottles. All bottles had previously been cleaned using bidistilled and de-ionized water. Throughout the sampling process, clean laboratory clothes and gloves were used. A short-circuit provoked by high water content below 35 m stopped drilling at 49.9 m.

Borehole temperature down to 45 m was measured using a Platinum resistive sensor (100 Ω at 0°C) previously calibrated and with a precision of ±0.05°C. Ice thickness was determined by a nearby radio echo-sounding survey that reached a depth of 314 m (Macheret et al. 1997, Macheret and Moskalevsky 1999), considered representative of the site.

Additionally three shallow-firn cores were recovered using a SIPRE 6-m drill at different altitudes (Figure 1, Table I); sampling and packing followed the same procedure of the main core. Finally, all samples were stored in the snow trench (mean temperature −3.5°C) until they could be transported to...
cold rooms in the Brazilian Navy polar vessel Ary Rongel, and then transported to LAPAG’s freezers in Porto Alegre, Brazil. Recently, LAPAG (Laboratório de Pesquisas Antárticas e Glaciológicas, Universidade Federal do Rio Grande do Sul) was re-structured as Núcleo de Pesquisas Antárticas e Climáticas (NUPAC), at the same institution.

LABORATORY INVESTIGATIONS

At LAPAG all the samples were melted in a clean room, a small volume was sent to the Laboratoire des Sciences du Climat et de l’Environnement (LSCE, CEA-Saclay, France) in sealed glass bottles for stable isotope analysis by mass spectrometry. At LSCE, a special purpose built mass spectrometer was used to determine δD (with a 0.15‰ precision) in 423 samples. A Finnigan MAT 252 spectrometer (0.5‰ precision) was used for measuring δ¹⁸O in 47 samples of the upper 6.7 m. Following standard practice, the stable-isotope content of both hydrogen and oxygen in a sample are expressed with reference to V-SMOW (Vienna Standard Mean Ocean Water). δ values were given from the following formula (Craig 1961a):

$$\delta x = \frac{R_{\text{sample}} - R_{\text{SMOW}}}{R_{\text{SMOW}}} \times 1000$$
TABLE I
Mean isotopic ratios at snow surface of KGI ice cap and in precipitation at Frei Station.
IC stands for the upper 2.7 m (water equivalent) at the KGI ice core sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Elevation (m a.s.l)</th>
<th>δD (‰)</th>
<th>δ¹⁸O (‰)</th>
<th>Excess-deuterium (‰)</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lange IC</td>
<td>690</td>
<td>–72.2</td>
<td>–9.7</td>
<td>5.6</td>
<td>34</td>
</tr>
<tr>
<td>Dome 2 IC</td>
<td>670</td>
<td>–77.1</td>
<td>–</td>
<td>–</td>
<td>19</td>
</tr>
<tr>
<td>Drake IC</td>
<td>600</td>
<td>–64.0</td>
<td>–</td>
<td>–</td>
<td>21</td>
</tr>
<tr>
<td>Ezcurra IC</td>
<td>575</td>
<td>–80.6</td>
<td>–</td>
<td>–</td>
<td>22</td>
</tr>
<tr>
<td>Frei precipitation</td>
<td>16</td>
<td>–77.6</td>
<td>–10.5</td>
<td>6.7</td>
<td>12</td>
</tr>
</tbody>
</table>

A Dionex 2000i with electrolytic conductivity detection, coupled to a Shimadzu C-R3A integrator, determined Cl⁻, SO₄²⁻ and NO₃⁻ concentrations in samples from the upper 9.0 m of the core (143 samples). Estimated concentration error was 8% and the detection limit was 10 ppb (i.e. ng g⁻¹) for the studied anions. To assess the extent of contamination during preparation, fieldwork and analysis, two blanks containing bi-distilled water, used to clean sampling bottles, were analyzed. Measurements were carried out at Laboratório de Saneamento Ambiental, Instituto de Pesquisas Hidráulicas (UFRGS), Bernardo (1999 unpublished) gives full details on the procedures for these analyses.

Snow and ice drilling chips were used to measure radionuclides. Twenty-five samples (5–10 kg each) were melted and filtered through ion exchange following the process described by Delmas and Pourchet (1977). In order to find peaks related to thermonuclear tests, Cs¹³⁷ content was measured by low-level gamma spectrometry (Pinglot and Pourchet 1994), providing a reference horizon for dating.

RESULTS

Stratigraphy and Density

Lange IC has a complex stratigraphy; ice layers of different thickness (mm to cm) are intercalated irregularly with snow and firm (Figure 4). Sections of the core show a high concentration of ice layers.
Fig. 3 – Sub-sampling the Lange IC, in a snow trench, under a portable laminar flow bench (background).

(Bold numbers from 1 to 9 in Figure 4). These observations are strong evidence that melting may occur at any time of the year. In high summer (February) superficial snow is wet even at 690 m a.s.l. in KGI (Braun et al. 2000). To the naked eye, no dust layers were observed. In short, stratigraphic information did not help the dating procedure. The firn-ice transition (density > 0.83 g cm$^{-3}$) occurs abruptly at 35 m depth (Figure 4) and is associated with a water table detected by a ground penetrating radar (GPR) survey at about 37 m (Travassos and Simões 2004, this volume).

Temperature

Borehole temperature, down to 45 m, varies from $-0.35$ to $-0.25^\circ$C and, at 11.20 m, it is $-0.27^\circ$C. Mean atmospheric temperature at the site is estimated to be about $-8.3^\circ$C, considering the mean annual temperature for the KGI temperature time series from 1945–95 ($-2.8^\circ$C; Ferron et al. 2004, this volume) and an adiabatic lapse rate of $-7.9^\circ$/km (Wen et al. 1994). The difference between the measured and estimated temperature denotes the intense refreezing at the site, resulting in the liberation of latent heat. Ice-rock interface is probably at the pressure melting point, as shown by several sediment plumes in Admiralty Bay (Aquino 1999 unpublished, Pichlmaier et al. 2004, this volume).

Stable Isotope Ratios

An upper interval (0.5 to 2.7 m, Figure 5a) shows the greatest $\delta D$ standard deviation (13.2‰%) and amplitude (57.6‰), mean values for $\delta D$ and $\delta^{18}O$ are $-72.2‰$ and $-9.7‰$, respectively (Table II). Isotopic homogenization is restricted, seasonal variations can be identified and, probably, still represent the original composition of the precipitation. Below 2.7 m, increasing homogenization of the stable isotopic variations is observed, reaching about 37% in the interval 2.7–14.9 m (mean $\delta D = -76.2‰$), further below it reaches 58% (mean $\delta D = -75.2‰$). Homogenization proportions were calculated in relation to the upper 2.7 m.
Figure 4 – Stratigraphic and density profiles along the 49.9 m long Lange IC. Depth scale (right) has been corrected for density. Numbers on the right side of the stratigraphic profile are the estimated years of deposition. Bold numbers from 1 to 9 correspond to zones with ice layer concentration.

Figure 6 compares δD variations in the upper part of the Lange IC with the record of three shallow cores recovered at different altitudes elsewhere on KGI ice cap (Figure 1). Table I shows a trend for higher isotopic ratios with altitude. Bearing in mind that in a relatively small ice cap, the precipitation originates from the same altitude and at the same temperature, thus, no trend should have been
TABLE II

Lange ice core $\delta D ($/$^{\circ}\!\!\!\!\circ$) at different depth intervals. "Homog." stands for the homogenization percentage of each section calculated in relation to the upper 2.7 m section.

<table>
<thead>
<tr>
<th>Depth interval (m water eq.)</th>
<th>Mean $\delta D$ ($^{\circ}!!!!\circ$)</th>
<th>Standard deviation ($^{\circ}!!!!\circ$)</th>
<th>Homog. (%)</th>
<th>Amplitude ($^{\circ}!!!!\circ$)</th>
<th>Minimum ($^{\circ}!!!!\circ$)</th>
<th>Maximum ($^{\circ}!!!!\circ$)</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5–2.7</td>
<td>–72.2</td>
<td>13.2</td>
<td>–</td>
<td>57.6</td>
<td>–108.0</td>
<td>–50.4</td>
<td>37</td>
</tr>
<tr>
<td>2.7–14.9</td>
<td>–76.2</td>
<td>8.4</td>
<td>37</td>
<td>43.1</td>
<td>–99.0</td>
<td>–56.7</td>
<td>155</td>
</tr>
<tr>
<td>14.9–34.9</td>
<td>–75.2</td>
<td>5.6</td>
<td>58</td>
<td>30.7</td>
<td>–90.1</td>
<td>–59.4</td>
<td>235</td>
</tr>
</tbody>
</table>

observed. The most probable cause for this altitude trend is that the sampled data refer to different time intervals. In other words, all-year precipitation had been sampled in the upper parts of the ice cap. In lower parts, the intervals are shorter and do not cover the summer precipitation.

IONIC CONCENTRATIONS

Based on the homogenization intensity, ionic profiles can also be divided in three sections: (1) 0.50 to 2.1 m water equivalent, (2) 2.1 to 25 m and (3) 25 to 34.9 m (Figure 5b-e). Below 2.1 m, all ionic records show strong signs of homogenization. The upper interval shows a high sulfate vs. chloride correlation (Figure 7, $r = 0.83, \alpha < 0.005$), strong evidence that this part of the record is representative of the original precipitation. No correlation between sulfates and chlorides was observed in the rest of the core.

Table III summarizes the mean results for all cores and for each section. Chloride concentration (Figure 5b) reaches up to 195.21 μEq L$^{-1}$. The upper preserved part has a mean chloride concentration of 120.40 ± 13.03 μEq L$^{-1}$. These relatively

Fig. 5 – Depth variation of analyses carried out for the 49.9 m Lange IC: (a) $\delta D$, (b) chlorides, (c) sulfates, (d) excess-sulfate, and (e) nitrates. Depth scale to the left has been corrected for density. Dotted lines mark subdivisions of the core based on the homogenization proportion.
high ionic concentrations are attributed to oceanic aerosols. Sea salt contributes to about 85% of the impurities found in the coastal Antarctic regions (Legrand and Mayewski 1997). Gas-particle conversion and anthropogenic pollution can also contribute to the HCl content, but these generally represent less than 1% of the total ionic charge in this region (ibidem).

Sulfate concentrations reach up to 100.83 µEq L$^{-1}$ (Figure 5c), but layers with no sulfate (detection limit 0.21 µEq L$^{-1}$) denotes a strong ionic flush out in the two deepest sections of the core. Mean concentration in the upper 2.1 m is 27.70 ± 7.07 µEq L$^{-1}$, this is almost four times that of the deepest section (8.01 ± 0.85 µEq L$^{-1}$). Oceanic aerosol is the major contributor to the high sulfate concentration in the upper 2.1 m of the Lange IC, about 57%. The maximum proportion of sea-salt is 90.5% (interpreted as a winter peak in the first 2 m of the core, Figure 5c). Excess-sulfate was calculated from the known sea-salt ratio of sulfates to chlorides, where $[SO_4^{2-}]^\ast = [SO_4^{2-}] - 0.103[Cl^-]$ (Mulvaney and Peel 1988). All calculations are carried out in µEq L$^{-1}$. Mean excess-sulfate in the upper 2.1 m is 15.26 ± 6.33 µEq L$^{-1}$ (Figure 5d).

Figure 5e shows the nitrate profile, with a mean value of only 0.88 ± 0.20 µEq L$^{-1}$. No nitrate was detected in the upper layers, peaks appear mainly in the interval from 5 to 25 m.

**ICE CORE DATING**

Seasonal variations in δD and ionic species (sulfates and chlorides) recognized in the upper 15 m of the Lange IC (Figure 5a-c) were used to date annual layers. The dated stable isotopic profile variations were compared with the δD profile from a James Ross Island ice core (Aristarain 1980 unpublished). Cesium-137 measurements were not conclusive due to low concentrations, probably due to intense flush out.

A relatively abrupt variation in the δD profile (the isotopic cold 1957–58), representing an El Niño year, fixes the Lange IC to the James Ross (Aristarain 1980 unpublished) and South Pole (Jouzel et al. 1979) core records.

The second, more polemic, was a Cs$^{137}$ peak found at 7.27 m. This peak (10 Bq m$^{-2}$) is low when compared to the mean flux over Antarctica (60 Bq m$^{-2}$) that is related to the 1962 and 1963 thermonuclear atmospheric testing recorded in the southern polar region in 1965 (Pourchet et al. 1997). This peak could have originated from nuclear testing carried out by China (1978) or France (1980). For example, a β-radioactivity anomaly is record in...
ICE CORE STUDY FROM KING GEORGE ISLAND, ANTARCTICA

TABLE III
Mean anionic concentrations at the surface of KGI ice cap. IC stands for the upper 2.1 m (water equivalent) at the KGI ice core sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Elevation (m a.s.l.)</th>
<th>Cl$^-$ (µEq L$^{-1}$)</th>
<th>SO$_4^{2-}$ (µEq L$^{-1}$)</th>
<th>Excess- SO$_4^{2-}$ (µEq L$^{-1}$)</th>
<th>NO$_3^-$ (µEq L$^{-1}$)</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lange IC</td>
<td>690</td>
<td>120.40</td>
<td>27.66</td>
<td>15.26</td>
<td>&lt; 0.21</td>
<td>13</td>
</tr>
<tr>
<td>Drake IC</td>
<td>600</td>
<td>857.55</td>
<td>118.00</td>
<td>29.67</td>
<td>19.84</td>
<td>8</td>
</tr>
<tr>
<td>Ezcurra IC</td>
<td>575</td>
<td>589.27</td>
<td>48.54</td>
<td>−12.16</td>
<td>24.44</td>
<td>8</td>
</tr>
</tbody>
</table>

James Ross Island in the winter of 1978 (Aristarain 1980 unpublished). On the other hand, peaks may have been created by the strong fixation capacity of the Cs with particulate impurities content in the snow. This may be the case in KGI because rock outcrops are found less than 5 km from the core site.

For the period before 1958, dating was carried out using a simple Nye’s model (Nye 1963). A mean net accumulation rate of 0.59 m a$^{-1}$ (after correcting for layer thinning) is considered representative for the core. The deepest layer is calculated to have been deposited in 1922 (an error of ± 4 years is estimated). Table IV summarises the dating results.

DISCUSSION

In Frei Station (Figure 1), precipitation in 1991 had mean annual δD and δ$^{18}$O of −77.6‰ and −10.54‰, respectively. These values were corrected for the precipitation amount. Mean values in the upper 2.7 m of Lange IC are higher (δD = −72.2‰, δ$^{18}$O = −9.7‰). The minimum at Frei station occurred in July (δD = −146.0‰, δ$^{18}$O = −20.0‰), and maximum in April (δD = −46.0‰, δ$^{18}$O = −6.5‰).

Figure 8a plots the δD vs. δ$^{18}$O relationship for precipitation samples from Frei Station, comparing with the linear relationship determined by Craig (1961b) for the meteoric water line (MWL). The equation (1) for the Frei Station samples is the following:

$$\delta D = 7.1 \delta^{18}O - 2.2^{\circ}/_{oo} \quad \text{with} \quad r = 0.99 \quad \text{for} \quad \alpha < 0.01$$

The regression slope is smaller than the one obtained by Craig (1961b); Moser and Stichler (1980)
TABLE IV
Dating of the Lange ice core based on δD and seasonal variations of ionic concentration compared with the results of a simple Nye’s flow model.

<table>
<thead>
<tr>
<th>Depth (m in water equiv.)</th>
<th>Accumulation rate (m a⁻¹)</th>
<th>Seasonal variation</th>
<th>Nye’s model</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8</td>
<td>2.0</td>
<td>0.51</td>
<td>1991, 1992</td>
</tr>
<tr>
<td>13.0</td>
<td>6.7</td>
<td>0.46</td>
<td>1980, 1981</td>
</tr>
<tr>
<td>15.4</td>
<td>8.2</td>
<td>0.50</td>
<td>1978, 1978</td>
</tr>
<tr>
<td>17.7</td>
<td>9.8</td>
<td>0.52</td>
<td>1975, 1975</td>
</tr>
<tr>
<td>21.8</td>
<td>12.5</td>
<td>0.51</td>
<td>1969, 1968</td>
</tr>
<tr>
<td>31.1</td>
<td>19.4</td>
<td>0.57</td>
<td>1958, 1956</td>
</tr>
<tr>
<td>35.0</td>
<td>22.3</td>
<td>0.57</td>
<td>1953, 1948</td>
</tr>
<tr>
<td>37.5</td>
<td>24.3</td>
<td>0.58</td>
<td>1950, 1944</td>
</tr>
<tr>
<td>39.9</td>
<td>26.3</td>
<td>0.58</td>
<td>1946, 1939</td>
</tr>
<tr>
<td>42.7</td>
<td>28.8</td>
<td>0.58</td>
<td>1940, 1933</td>
</tr>
<tr>
<td>45.3</td>
<td>30.9</td>
<td>0.59</td>
<td>1936, 1928</td>
</tr>
<tr>
<td>48.3</td>
<td>33.6</td>
<td>0.59</td>
<td>1929, 1922</td>
</tr>
<tr>
<td>49.9</td>
<td>35.0</td>
<td>0.59</td>
<td>1926, 1918</td>
</tr>
</tbody>
</table>

concluded that slopes significantly different from 8 indicate a fractionation process under no-thermo-dynamic equilibrium. Equation 1 does not differ considerably from the MWL, therefore it is reasonable to suppose that air masses reach KGI under conditions stated by Cias and Jouzel (1994), where vapor, liquid and solid phases co-exist in the clouds, and where precipitation is made of ice crystals and supercooled water droplets.

Plotted points show little dispersion from the regression line in Figure 8a. Four groups can be identified and they point out air masses of different origin, bringing in precipitation during the year. Groups 1 and 2 have the highest isotopic values; δD = -53.3‰ and δ¹⁸O = -6.8‰ (Group 1), δD = 61.3‰ and δ¹⁸O = -9.2‰ (Group 2) and indicate a moisture source near KGI. Group 4 with the lowest values (δD = -136.7‰ and δ¹⁸O = -18.7‰) probably represent air masses that followed a longer pathway due to the expansion of winter sea ice.

The sample position in the diagram δD vs. δ¹⁸O is a function of: (1) the initial vapor composition; (2) the difference between the evaporation and condensation; (3) the cooling type (e.g. isobaric or adiabatic), (Dansgaard 1964). In KGI, due to the high relative air humidity, the stable isotopic exchange between precipitation and atmospheric water vapor may be an important factor for a slope different from 8 in the δD vs. δ¹⁸O relationship.

The four precipitation groups are also found in the Lange IC isotopic record (Figure 8b). In this graphic only the points from the upper interval (0.5 to 2.7 m) were plotted. It is to note that the core regression line (Equation 2) has the same slope as in the Frei Station samples:

$$\delta D = 7.1 \delta^{18}O - 3.1 \% $$ with

$$r = 0.98 \text{ for } \alpha < 0.01$$ (2)

The similarity between equations 1 and 2, reinforces the hypothesis of an upper Lange IC core with week post-depositional isotopic fractionation.

Sulfate and chloride concentration in KGI snow and ice are at least one order of magnitude greater than values found on the Antarctic Peninsula and agree with observations at Marsh station on Fildes Peninsula (Minikin et al. 1998), and with concentrations found in an ice core taken in 1991, by the Chinese Antarctic Expedition (CHINARE), from a nearby site on the KGI ice cap (Han et al. 2001).
These relatively high concentrations result from several factors: (1) a relatively warm coast, when compared to the cold and more stable atmospheric circulation in the eastern Antarctic Peninsula; (2) a restricted sea-ice extent. In some years, during the 1990s, Admiralty Bay did not totally freeze over; (3) low altitude (the highest point in KGI is about 707 m a.s.l.); (4) proximity to the sea (at about 7 km distance), with mechanical formation of oceanic aerosols (associated to high velocity winds and frequent cyclonic activity with high relative humidity). These high concentrations are also observed in aerosol studies (Savoie et al. 1993, Correia 1998 unpublished) and a rain water collection at the Brazilian Comandante Ferraz Station (Moreira-Nordemann et al. 1989). Cl$^-$ and Na$^+$ make up approximately 84% of the ionic total (Wen et al. 1998).

The high excess-sulfate concentrations mask any evidence of local anthropogenic pollution (e.g. due to hydrocarbons burning in 9 KGI stations). Excess-sulfate in Antarctica may originate from H$_2$SO$_4$ ejected in the atmosphere by volcanic eruptions and by pholitic oxidation of sulfur gases. These gases (mainly SO$_2$) originate primarily from dimethyl sulfate (DMS). DMS is produced by marine biota (Legrand et al. 1997) and is the main volatile sulphured compound from the superficial layer of the ocean. DMS peak production is dur-
ing summer months, being minimal in winter. On the other hand, the high excess-sulfate peak values found in the Lange core may be just an artifact from the way that it was estimated (indirectly from the sea-salt ratio of sulfates to chlorides). Partial melting is observed on the surface of the ice cap and this causes preferential SO$_4^{2-}$ elution (i.e. it flushes out downward before the Cl$^-$), leaving layers with negative excess-sulfate. Further down, positive peaks of excess-sulphate is found, as the snow layers are enriched with SO$_4^{2-}$ (Note that we did not sample the first meter at the surface). This process is known to happen, for example, in the southern Patagonian ice cap (Aristarain and Delmas 1993).

Nitrate peaks found below the 5 m depth of the Lange IC may be explained either by (1) nitrate formation linked to gas-particle conversion of NO$_x$ species in the stratosphere and upper troposphere (Parker et al. 1982, Legrand and Delmas 1986, Legrand and Kirchner 1990); or by NO$_2$ brought from South America by warm air masses (Moreira-Nordemann et al. 1989). Marine contribution may be small; Admiralty Bay surface water (upper 50 m) shows nitrate concentrations of only 16.0 to 24.0 $\mu$Eq L$^{-1}$ (Moreira-Nordemann et al. 1989).

The mean net accumulation rate recorded for Lange IC (0.59 m a$^{-1}$) is about one quarter of the rate calculated for the nearby Chinese ice core (2.48 m a$^{-1}$). On the other hand, Ferron (1999) and Bernardo (1999 unpublished) observed that the Lange IC, in the period 1957–1994, shows mean annual accumulation rates highly variable, oscillating from 0.1 to 1.2 m a$^{-1}$ water equivalent. He observed that high accumulation years coincide with El Niño years.

**CONCLUSIONS**

Stable isotope ratios, anionic content and stratigraphic evidence show that KGI ice cores are strongly altered by post depositional phenomena (i.e. partial melting, percolation and refreezing). In these cores, damping of the anionic seasonal variations and isotopic homogenization are frequently, a consequence of a relatively warm summer, typical of a maritime subpolar environment. On the other hand, the upper meters of the highest ice core (Lange) still conserves seasonal variations of the measured variables, providing the reference for the background chemical composition in the South Shetlands ($\delta D$: $-72.2^\circ$, $\delta^{18}O$: $-9.7^\circ$, Cl$^-$: 120 $\mu$Eq L$^{-1}$, SO$_4^{2-}$: 28 $\mu$Eq L$^{-1}$, excess-SO$_4^{2-}$: 15 $\mu$Eq L$^{-1}$). The isotopic composition and the $\delta D$-$\delta^{18}O$ relationship of the upper part of Lange IC are similar to the precipitation values. Furthermore, the four isotope groups found in the precipitation can be recognized in the core samples.

Stable isotope seasonal variations are recognized down to 15 m allowing for the determination of the mean net accumulation rate (0.59 m a$^{-1}$ water equivalent). The Lange IC represents about 73 years of precipitation. Yearly net accumulation rate at the top of the KGI ice cap is highly variable and further studies are needed to check if there is any correlation to El Niño events.

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que a transição firn-gelo ocorre a 35 m de profundidade. O registro ambiental é homogeneizado devido ao intenso derretimento superficial, seguido por percolação e recongelamento. Abaixo de 37 m de profundidade, o registro foi intensamente lavado por um aquífero intraglacial. Por outro lado, os 2,7 m superiores são considerados representativos da precipitação original, e provêm valores de referência da composição química de fundo nas Shetlands do Sul ($\delta^{18}O$: $-72\,^{\circ}/_{\circ}$, $\delta^{2}D$: $-9\,^{\circ}/_{\circ}$, $\mathrm{Cl}^{-}: 120\,\mu\text{Eq L}^{-1}$, $\mathrm{SO}_{4}^{2-}: 28\,\mu\text{Eq L}^{-1}$, e excesso de $\mathrm{SO}_{4}^{2-}: 15\,\mu\text{Eq L}^{-1}$). Variações sazonais nas razões de isótopos estãoveis são reconhecidas até 15 m de profundidade e permitem a datação do testemunho. Abaixo desta profundidade, foi utilizado um modelo simples de Nye, resultando em uma taxa de acumulação líquida média de 0,59 m a$^{-1}$ (em equivalente de água) ao longo de 73 anos de precipitação.

**Palavras-chave:** Glacioquímica, estratigrafia do gelo, registro ambiental, calota de gelo, Shetlands do Sul.

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