Glaciochemical Investigations in Three Southern Hemisphere Mountain Sites

Mariusz Potocki

University of Maine, mariusz.potocki@maine.edu

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GLACIOCHEMICAL INVESTIGATIONS IN THREE SOUTHERN HEMISPHERE MOUNTAIN SITES

By

Mariusz Potocki

M.S. University of Warsaw, 2004

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy (in Earth and Climate Sciences)

The Graduate School
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August 2022

Advisory Committee:

Paul A. Mayewski, Director/Professor at Climate Change Institute, Advisor
Andrei V. Kurbatov, Associate Professor at Climate Change Institute, ECS
Kirk A. Maasch, Professor at Climate Change Institute, ECS
Sean Birkel, Assistant Extension Professor at Climate Change Institute
Jefferson C. Simões, Professor at the Federal University of Rio Grande do Sul
GLACIOCHEMICAL INVESTIGATIONS IN THREE SOUTHERN HEMISPHERE MOUNTAIN SITES

By Mariusz Potocki

Thesis Advisor: Dr. Paul A. Mayewski

An Abstract of the Thesis Presented in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy (in Earth and Climate Sciences) August 2022

The research presented in this dissertation focuses on glaciochemical records of trace elements, major ions, and stable water isotopes from three mountain regions: the Antarctic Peninsula, the Central Chilean Andes, and South Georgia Island.

The first section reports a significant increase in U concentration over 27 years on Detroit Plateau, Antarctic Peninsula. U concentrations in the ice core increase by as much as 10^2 between the 1980s and 2000s, accompanied by increased variability in recent years. The U concentration increase coincides with expanded open pit mining in the Southern Hemisphere, most notably Australia. Since other land-source dust elements do not show similar large concentration increases, and since the increased U concentrations are enriched above average levels in the Earth's crust, the source of U is attributed to human activities rather than atmospheric circulation changes.

The second section of this dissertation presents a 100-year, continuous, sub-annually dated ice core record from Tupungatito glacier, Central Chilean Andes. This section documents change over time of atmospheric pollution in Central Chile and a significant change in atmospheric pollutant concentrations coincident with anthropogenic activities in this region. Moreover, Cd, As, Pb, Cu, and Ag concentrations exhibit enriched values far in excess of natural levels over the last
century, with the increases beginning around the 1930’s.

Lastly, the third section of thesis dissertation focuses on a short glaciochemical record from a snow/firn core collected on South Georgia Island. This reconnaissance study provides information about snow chemistry and preservation of environmental records at an elevation of 850 m a.s.l. The results presented in this section help to determine the feasibility of future deep ice coring on South Georgia Island.
DEDICATION

I dedicate this dissertation to Marta, Jan, and Julia.
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CHAPTER 1
INTRODUCTION

Both naturally and anthropogenically forced climate change have a dramatic impact on humans and ecosystems. The study of past climate variability from ice cores has been largely conducted in the polar regions with less attention to mountain glaciers. As a result of recent warming, however, many mountain glaciers suitable for robust reconstructions of climate and environmental change records are rapidly disappearing, taking with them unique paleoenvironmental information stored in the ice (Potocki, Mayewski, et al., 2022).

Trace and heavy metals occur naturally in the environment in small concentrations, but human activities including industry, agriculture, mining, construction and large-scale land use release these metals in concentrations greater than natural background levels (Nriagu & Davidson, 1985). These metals, particularly as fine particles, are transported within air-masses from their emission sources and subsequently can accumulate far from their source regions. Their presence has potentially adverse effects on the environment and human health (Pacyna & Pacyna, 2001). The primary source of heavy metals and trace elements in the atmosphere is the transport of dust emitted during surface mining and milling operations (Barbante et al., 2001). South Hemisphere emissions of trace and heavy metals are increasing as a result of increasing population, agriculture, and industrial production.

In this dissertation, I examine glaciochemical variability using snow/firn and ice core chemistry from three mountain regions: the Antarctic Peninsula, Central Chilean Andes, and South Georgia (Figure 1.1).
Figure 1.1. Study sites: Tupungatito in Central Chilean Andes, Detroit Plateau on the Antarctic Peninsula, and the South Georgia.

1.1. Recent increase in Antarctic Peninsula ice core uranium concentrations

Understanding the distribution of airborne uranium is important because it can result in both chemical and radiological toxicity. In Potocki et al. (2016) we present the first sub-annually dated, continuously sampled ice core documenting change in U levels in the Southern Hemisphere. The ice core was recovered from the Detroit Plateau, northern Antarctic Peninsula, in 2007 by a joint Brazilian-Chilean-US team. It displays a significant increase in U concentration that coincides with reported mining activities in the Southern Hemisphere, notably Australia. Raw U concentrations in the Detroit Plateau ice core increased by as much as $10^3$ between the 1980s and 2000s accompanied by increased variability in recent years. Decadal mean U concentrations increased by a factor of $\sim 3$ from 1980-2007, reaching a mean of 205 pg/L from 2000 to 2007. The fact that other terrestrial source dust elements such as Ce, La, Pr, and Ti do not show a similar
increase and that the increased U concentrations are enriched above natural crustal levels, supports an anthropogenic source for the U as opposed to a change in atmospheric circulation.

1.2. Trace metal emission history captured in a Chilean ice core

In Potocki et al. (2022) we present a sub-annually dated, continuously sampled Tupungatito ice core (TPG-12) data set that documents change in atmospheric pollution in Central Chile. Results from this well-preserved environmental record display a significant change in atmospheric pollutant concentrations coincident with anthropogenic activities in this region, notably from Chile. TPG-12 Cd, As, Pb, Cu, and Ag exhibit values in excess of natural inputs over the last one hundred years, with increases beginning around 1930. Terrestrial source dust elements such as Ce, La, Pr, and Ti do not exhibit similarly increased values, demonstrating an anthropogenic source for Cd, As, Pb, Cu, and Ag. Our results also capture a decrease in As and Pb starting in the early 2000s, in concert with new environmental regulations in Chile (Caldentey & Mondschein, 2003a).

1.3. South Georgia ice core reconnaissance

In 2015 we recovered a continuous 15.4 m snow/firn core from central South Georgia at ~850 m a.s.l.. Ground-penetrating radar (GPR) indicates that the ice thickness is ~400 m at the core site. All ice core samples were analyzed for major and trace element concentrations (Sr, Cd, Cs, Ba, La, Ce, Pr, Pb, Bi, U, As, Li, Al, S, Ca, Ti, V, Cr, Mn, Fe, Co, Na, Mg, Cu, Zn, and K) and stable water isotopes. The chemical and isotopic signal is well preserved in the top 6.2 m of the core and below this depth, down to the bottom of the core, all soluble and some elemental species are affected to some degree by wash-out making it difficult to distinguish a seasonal signal below 6.2 m depth. Thirteen elements (As, Bi, Ca, Cd, Cu, K, Li, Mg, Na, Pb, S, Sr, and Zn) have values
higher greater than those naturally in the crust. Add cesium finding in here While this study shows that 850 m a.s.l. is not high enough to preserve a record including recent years, higher-elevation (>1250 m a.s.l.) glaciers may be likely candidates for ice core drilling to recover well-preserved, continuous, recent to past glaciochemical records, particularly since annual layers appear to be persevered in old ice recovered in a previous study (Mayewski et al., 2016) from the terminus of South Georgia glacier.
CHAPTER 2
RECENT INCREASE IN ANTARCTIC PENINSULA ICE CORE URANIUM CONCENTRATIONS


2.1. Introduction

Uranium can result in both chemical and radiological toxicity although there are currently no reference concentrations available for evaluating risk assessment for inhaled uranium exposure. Previous work (Planchon et al., 2002a, 2002b) ascribed recent elevated U concentrations in Antarctica to anthropogenic sources. There are, however, few published records of U concentrations in Antarctic ice and snow and none that offer continuous, sub-annually resolved time series that can be compared and traced directly to modern anthropogenic sources.

Continental dust, volcanism and sea spray are the main natural sources of U to the atmosphere (Planchon et al., 2002a; Vallelonga et al., 2004). While the contribution of natural sources to total concentrations of U can be estimated based on calculation of natural abundances, it has thus far been difficult to quantify the contributions of individual natural and anthropogenic sources (Planchon et al., 2002a, 2002b). Until WWII, the vast majority of U input to the atmosphere was from natural sources. Since 1945, increases in Southern Hemisphere U levels have been assumed to be attributed to U mining in South Africa, Namibia and Australia (Brown et al., 2010; Planchon et al., 2002b).

To establish natural, preindustrial background concentrations of U, we examine a suite of Antarctic ice core records shown in Figure 2.1. In the Law Dome (East Antarctica) ice core, all of
the U is assumed to be of rock dust origin with mean U concentrations of 25.6 pg/L for the period 4500 BC to 1989 AD based on 31 individual firn- and ice-core samples (Vallelonga et al., 2004). A suite of ice cores and snow pits (Figure 2.1.) from interior Antarctica demonstrate that mean U concentrations from 1955 to 2006 do not exceed 169 pg/L (Dixon et al., 2013). A snowpit from Coats Land shows elevated levels of U in recent decades relative to the early 1800s, but a source for the elevated U levels is not suggested (Planchon et al., 2002a). Finally, the SPRESSO ice core from South Pole exhibits a mean U concentration of 104.07 pg/L from 1971 to 1999 with no apparent trend.

Figure 2.1. Location of DP-07-1 ice core drilling site in Antarctica. Also shown are locations of the US ITASE-02-1, 02-5, 02-6, 03-1, 03-3, 06-2, 07-4 (pink dots US ITASE-02 traverse, orange dots US ITASE-03 traverse, green dots US ITASE-07 traverse; Dixon et al., 2013) and Coats Land
(Planchon et al., 2002a, 2002b), and Law Dome (Vallelonga et al., 2004) snow pit sampling and
firn/ice core drilling sites discussed in this paper.

2.2. Methodology

2.2.1. Ice Core Collection and Chemical Analysis

In this study we use a 133m deep ice core (DP-07-1; 64.05°S, 59.39°W) recovered in 2007
from the Detroit Plateau (DP) by the Joint Brazilian-Chilean-USA expedition as part of the
Scientific Committee for Antarctic Research CASA (Climate of the Antarctic and South America)
and ITASE (International Trans Antarctic Scientific Expedition) research initiatives. DP is located
in the northern part of the Antarctic Peninsula (Figure 2.1.) and has a mean elevation of ~1900 m
m.a.s.l. On the basis of borehole measurements, the temperature of the DP ice cap at 10m depth
is approximately -14 °C and very few melt layers were observed in the firn, thus assuring a well-
preserved record. Mean annual accumulation is on average 2.5 m w.e. for the last 27 years
allowing for sampling resolution sufficient to document seasonal and higher frequency variability.
Based on the foregoing, the upper 98 m of this core was processed using ultra-clean handling
procedures (Mayewski et al., 1986), yielding a high resolution (average 36 samples/year) U record
covering the period 1980-2007 compared to the Coats Land and Law Dome records that have a
much lower resolution (several samples per decade).

To prevent the incorporation of secondarily introduced contamination from drilling, ice
core packing, and handling the DP ice samples were scraped inside a HEPA clean hood (-20°C)
using a clean ceramic knife. Samples for trace-element analysis were collected directly into acid-
cleaned (10% trace metal grade HNO3) polypropylene Nalgene jars. Before analysis each sample
was acidified to 1% with Optima double-distilled HNO3 under a class-100 HEPA clean bench and
left to digest for 60 days. All samples were analyzed for major and trace elements (Sr, Cd, Cs, Ba, La, Ce, Pr, Pb, Bi, U, As, Li, Al, S, Ca, Ti, V, Cr, Mn, Fe, Co, Na, Mg, Cu, Zn, and K) using the Climate Change Institute Thermo Electron Element2 ICP-SFMS. Samples were analyzed using a Elemental Scientific Apex Q with nitrogen addition and a self aspirated ESI PFA-ST nebulizer with a sample uptake of 100ul/min. U-238 was measured in low resolution and was calibrated before each sample run with a calibration ranging from 10 – 1000 pg/L. The U method detection limit was 6.46 pg/L and was calculated by measuring 7 process blanks and calculated as three times the standard deviation of process blanks (E. C. Osterberg et al., 2006).

2.2.2. Dating of the Ice Core

The DP-07-1 depth-age scale is based on a well-preserved, well-defined seasonal signature in photochemically-produced hydrogen peroxide (Figure 2.4a) with highest and lowest values representing the summer and winter solstice, respectively (Frey et al., 2006). The stable water isotope deuterium (δD) record from DP does not have a clear enough seasonal variability to yield annual signals and as a result it was not useful for ice core time scale development (Figure 2.2.).
2.3. Results

2.3.1. Variation in Uranium Concentrations for The Period 1980-2007

Mean U concentrations in the DP ice core increase from 70 pg/L in the 1980s, (Figure 2.5b) to 90 pg/L in the 1990s, ultimately reaching 205 pg/L between 2000 and 2007. Overall there is a factor of ~3 increase in mean U concentration during the period 1980-2007. During the 1980s, there is less variability in the U concentrations compared to 1990-2007. Raw U values range from
10 pg/L to 610 pg/L in the 1980s and from 6 pg/L to 1900 pg/L in 1990-2007. To determine if sampling resolution (decreasing with depth) plays a role in the observed differences, we resampled the U data to seasonal resolution (4 samples/year). Seasonal U values range from 23 pg/L to 180 pg/L during the 1980s and from 26 pg/L to 500 pg/L during 1990-2007 maintaining the notable difference in concentration between the two periods.

2.3.2. Flux Values

The Gomez ice core record (Figure 2.1.) collected 1150 km south of DP-07-01 near the base of the Antarctic Peninsula, reveals an increasing trend (over the last 150 years) in annual snow accumulation (Thomas et al., 2008, 2009). An increasing trend is also captured in the DP-07-1 snow accumulation record (Figure 2.4c). In DP-07-1, the covarying and increasing snow accumulation and U concentrations result in large U annual depositional flux values (flux = concentration × accumulation rate/per unit area). Since the flux calculation only magnifies the relationship and does not affect the overall trend in the data we use concentration for the remainder of this study.

Net snow accumulation rate changes on the Antarctic Peninsula are attributed to an intensification of the transport strength of the westerlies (Abram et al., 2011; Thompson & Solomon, 2002; Turner et al., 2005). To test whether U concentration increases are caused by intensified atmospheric transport or an increase in U source emission strength, we examine the behavior of other terrestrial and marine source chemical tracers in the DP-07-1 record. Crustal (Ce, La, Pr and Ti) and marine (Na and Sr) tracers do not show a significant background concentration increase since 1980 (Figure 2.3). Therefore, the observed rise in U cannot be attributed to an increase in crustal dust or marine-source aerosols.
Figure 2.3. DP-07-1 Ce, La, Pr, Ti (ng/L), Na (μg/L) and Sr (ng/L) concentration from 1981 to 2007. Lack of trend in the recent portion of the record demonstrates that the U rise is not related to an intensification of atmospheric circulation. If this were the case all of the foregoing would rise with U.
Figure 2.4. DP-07-1 (a) H2O2 molar concentration (µM); (b) U concentration (pg/L); (c) annual accumulation in water equivalent (m); (d) U mean crustal enrichment factor (EFc) values and (e) mean non oceanic U crustal enrichment factor values; (f) Australian (brown), Namibian (green) and South African (pink) uranium production (tonnes); (g) excess U (% of total U concentration).
The light color lines in concentration and enrichment factor profiles are raw data and the dark color lines are the 9-point smooth data.

### 2.3.3. EOF Analysis

EOF (empirical orthogonal function) analysis of DP-07-1 chemistry data is used to reveal common associations such as sources, transport, and timing (Table 2.1.). EOF analysis is a mathematical decomposition of a data set in terms of orthogonal basis functions (EOF modes) that are determined from the data. EOFs are designed to capture temporal variance using as few modes as possible.

| Table 2.1. EOF table of trace elements and H$_2$O$_2$ as measured in the DP-07-1 samples. The numbers in the table represent the percent of variance associated with each major element/ H$_2$O$_2$. |
Using this approach, we interpret EOF 1 as a dust signal because it is composed primarily of crustal elements (31% of the Total Variance Explained (TVE)). EOF 1 also accounts for 41% of the total U signal. We interpret EOF 2 as a marine signal because it is composed primarily of marine elements (22% TVE). However, EOF 2 only accounts for 2% of the total U signal (Table 2.1.). Most of the remaining U signal is captured by EOF 9 (2% TVE) and EOF 12 (2% TVE), representing 21% and 20% of the total U, respectively. EOF 9 and EOF 12 are represented almost exclusively by U, and in contrast to EOF 1 and EOF 2, EOF 9 and EOF 12 display significant increases since 2000 AD (Figure 2.5.). Therefore, we conclude that EOF 9 and EOF 12 capture the non-marine, non-crustal sources of U.

![Figure 2.5.](image)

**Figure 2.5.** Comparison of DP-07-1 trace elements and H$_2$O$_2$ variance, from 1981 to 2007, as represented by EOF1, EOF9 and EOF12.
2.3.4. Crustal and Oceanic Enrichment Factors

To elucidate potential sources, we calculate a mean Enrichment Factor (EF) for U (Figure 2.2d) using methodology similar to Osterberg et al. (E. Osterberg et al., 2008). Using mean upper crustal (Wedepohl, 1995) and oceanic (Lide, 2005) elemental abundances, we estimate the average crustal EF (EFc) and average oceanic EF (EFo) such that: EFc = ([U/r]sample/[U/r]upper crust), where r is one of the conservative crustal elements: Ce, La, Pr, and Ti. The final EFc for U is the mean EFc from these four elements. The ice core drill was made out of Al; therefore, we do not use Al as a conservative crustal indicator. EFo for U is calculated using the same method as EFc using Na and Sr as conservative marine source elements.

Calculated EFc and EFo values up to 10 are considered to be almost entirely from crustal and oceanic sources, respectively, and allow for the natural regional fluctuations on Earth (Duce et al., 1975; Planchon et al., 2002a; Vallelonga et al., 2004). EF values greater than 10 are assumed to indicate a strong additional source. The mean EFc over the past 150 years in the Coats Land study (Planchon et al., 2002a) was 1.8 with a mean EFc of 4 and a maximum EFc of 9 over the 1959-1990 period. This is indicative of primarily natural sources of U reaching Coats Land up until 1990. From 1980 to 1990, the DP-07-1 mean EFc value is 6. From 1990 to 2008 the DP-07-1 mean EFc is 15, with a maximum value of 370 (Figure 2.2d).

Ocean spray can contribute a significant amount of U to Antarctic coastal sites (Dixon et al., 2013; Toggweiler & Russell, 2008; Vallelonga et al., 2004). We calculate the ocean water fraction of U according to the following formula: oceanic fraction for U (Uo = mean(rsample·[Uocean/rocean]), where r = Na and Sr). Then we subtract Uo from our total U to get non-oceanic U. We then calculate the non-oceanic U EFc values. Although slightly lower as a consequence of the foregoing, the majority of the non-oceanic U EFc values are still highly
enriched (i.e. EFc >10) from 1990 to 2008, and the trend of increasing enrichment is unchanged (Figure 2.2e).

2.3.5. Excess Uranium Concentration

To partition the natural and anthropogenic sources of U, we calculate the excess (xs) U concentration. To determine xsU (i.e. the U contribution from sources other than crustal dust and ocean spray), we calculated Uo and Uc and subtracted them from the raw U concentrations. The xsU concentrations indicate that significant (in many cases >60%; Figure 2.2g) additional U inputs occur after 1990, likely from anthropogenic sources.

2.4. Discussion

In order to assess the possible contribution by U mining to U loading in the DP ice core, we examine all available historical data on Southern Hemisphere U mining operations. Major above-ground mining operations and U ore processing in the Southern Hemisphere take place in Namibia, South Africa and Australia (World Nuclear Association, 2014). Australian U production (Figure 2.2f) matches closely with DP-07-1 U concentrations and xsU values, further validating U mining as a potential primary anthropogenic U source. The other major producers of U in the Southern Hemisphere, Namibia and South Africa (Figure 2.2f), show a marked decrease in U production since the early 1980s. Because the measured U concentration trend in DP-07-1 is inverse to the Namibian and South African long-term U production trends, we conclude that these sites likely do not constitute a significant source of U for the Antarctic Peninsula. Further, high DP-07-1 xsU (Figure 2.2g) between 1989 and 1993 are followed by a return to baseline values until ~1996. This return to baseline coincides with a reduction in Australian U production. The
increase in Australian U production from 1996 to 2008 also coincides with increasing DP-07-1 xsU. This is in contrast to a weak rise in Namibian U production over the same period and a continued slow decline in South African U production, further highlighting Australia as the most likely anthropogenic U source for the Antarctic Peninsula.

Sub-annual deposition timing of U in DP-07-1 may be related to rainfall seasonality in the vicinity of major Australian U mining centers. To investigate this possibility, the xsU record was resampled to 2-monthly resolution using the summer maxima and winter minima H2O2 values for each year and dividing each half-year into 3 equally-spaced intervals. The sub-annual maximum in the DP-07-1 xsU record appears during July-August when mean monthly rainfall over Australian mining regions (e.g. Ranger Mine and Olympic Dam Mine) is at a minimum (Figure 2.6.).
Figure 2.6. Comparison of mean excess U concentration (pg/L) resampled to two month intervals with mean (1971-2013) monthly rainfall (mm) in Ranger Mine (Jabiru Airport), Northern Australia.

During austral winter, mean rainfall values for the Olympic Dam region in South Australia are often below 3mm per month. During such dry periods, large volumes of dust can enter the atmosphere and subsequently are transported with the westerlies to the Antarctic Peninsula (Li et al., 2008). This process conceivably occurs as dry soils in these subtropical and dry-season tropical locations are subjected to dry convection resulting in lifting of dust to higher altitudes. In winter (Figure 2.7) the circumpolar westerlies attain their most equatorward position, particularly over Australia where they comprise the subtropical jet stream (STJ). Previous work suggests that it takes 3 to 10 days for dust to reach Antarctica from Patagonia or Australia (Krinner & Genthon, 2003; Sudarchikova et al., 2014). Thus, the fast mid-troposphere flow accompanying the STJ over Australia and its associated southern branch (middle-latitude jet) could explain the rapid transport of U to Antarctica. Separating the recent period into two approximately equal-length sub-periods (1981-1994, 1995-2007) suggests that the more recent strong increase in U measured at DP-07-1 is unlikely to be the result of more rapid transport in the mid- to upper-troposphere over Australia since the STJ was weaker in the second sub-period (Figure 2.8.). It is also suggested that only South America and Australia commonly spawn air masses that reach the Antarctic within 30 days of transport from source (Albani et al., 2012; Dixon et al., 2012). However, there was very little U mining in South America over the period of record in this study.
Figure 2.7. Seasonal long-term (1981-2007) averages of 500 hPa winds (direction: arrows; speed: color shading) for the eastern portion (0° - 180° longitude) of the Southern Hemisphere: (a) summer, DJF; (b) autumn, MAM; (c) winter: JJA; (d) spring, SON.
To further prove that South American air masses seldom reach the study site, we assess air mass origin at DP. We use ERA-Interim Reanalyses data (Dee et al., 2011) to plot a wind rose diagram (Figure 2.9.) of monthly mean wind speed and direction over the 1981 to 2007 period. The wind rose shows westerly winds to be dominant over this time period.
Figure 2.9. Wind rose diagram of monthly mean wind speed and direction for Detroit Plateau over the 1981 to 2007 period (ERA-Interim Reanalysis data).

Additionally, we perform Hysplit (Rolph et al., 2017; Stein et al., 2015) back-trajectory cluster analysis for each season during 2004, which is a high U-concentration year in the DP chemical record. Back trajectories were calculated over a period of 20 days and multiple trajectory iterations were run from DP. These iterations were run every 6 hours for 10 days resulting in 40 back trajectories clustered for each season. We chose the middle month of each season for each
run (i.e. October for SON, January for DJF, etc.). The cluster analysis results (Figure 2.10.) show that during the period of maximum U deposition (JJA; Figure 2.6), the majority of the air masses reaching DP are coming from the west.

![Figure 2.10](image_url)

**Figure 2.10.** Cluster analysis of back-trajectories calculated by the HYSPLIT transport model - (a) January, (b) April, (c) July, (d) October.

Empirical Orthogonal Function analysis shows that the mean annual rainfall, Australian U production, and DP U Concentration are all positively associated in EOF 1 (total variance explained by EOF 1 = 55%) at 65%, 74%, and 74% respectively (Table 2.2). This result shows that DP U Concentrations are most strongly associated with Australian U production. However,
it is also worth noting that despite an increase in mean annual rainfall (Figure 2.11.) over the Australian open pit U mining region, DP U concentrations are still increasing.

<table>
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*Table 2.2. EOF table of Australian U production, DP mean U concentration (pg/L), Jabiru annual rainfall (mm) and Southern Pacific Annual Zonal Wind Speed (m/s) from 1981 to 2007. The numbers in the table represent the percent of variance associated with each component.*
Figure 2.11. Comparison of Southern Pacific mean zonal wind speed, mean annual rainfall in Jabiru, DP U concentration, and Australian U production, with EOF1 from 1981 to 2007.
2.5. Conclusions

Our study provides the first continuous, high-resolution record of U concentrations from an Antarctic Peninsula ice core. We report significant U increases in the atmosphere over the last two decades. Australia is the most likely source of U pollution captured by this 27-year Antarctic Peninsula snow archive. Therefore, we conclude that U deposition at DP is likely related to U mining operations in Australia.

This study demonstrates that dramatic levels of anthropogenic source pollution from Southern Hemisphere industrial sources, in this case open pit mining, are impacting at least the northern fringes of the Antarctic continent. Impacts of this exposure on Antarctic ecosystems are yet to be determined, but they should now be considered. Baseline investigations of the distribution of human source pollutants are essential to understanding changes in human and ecosystem health. Finally, DP offers a good monitoring platform for assessing changes in Southern Hemisphere source pollutants entering Antarctica.
CHAPTER 3

TRACE METAL EMISSION HISTORY CAPTURED IN A CHILEAN ICE CORE


3.1. Introduction

Since the mid-1950’s, ice cores have been used extensively as tools to study past climate variability in the polar regions. More recently, ice cores have also been recovered from high mountain glaciers (Ginot et al., 2006; Knüsel et al., 2003). Despite these efforts, a large data gap remains in the Southern Hemisphere mid-latitudes (Bolius et al., 2006; Ciric et al., 2009). Paleoenvironmental records such as the Tupungatito ice core (TPG-12) provide data that improve our understanding of local and global trends, in particular with respect to the relative contributions of natural and anthropogenic emissions into the atmosphere, as shown by previous ice core studies in the Southern Hemisphere (Hong et al., 2004; Korotkich et al., 2019; Schwanck et al., 2016).

Tupungatito glacier is located in an actively outgassing strato-caldera in the central Chilean Andes (Figure 3.1.) at an altitude between 5400m and 5750m a.s.l. where seasonal snowfall is well-preserved. Climate in the region is dominated by the quasi-permanent influence of the South Pacific High Pressure center, and the seasonal north-south displacement of the westerlies that direct frontal depressions towards central Chile during the winter (Vimeux, Ginot, et al., 2009). Tupungatito receives the majority of its precipitation from frontal systems that develop in the Pacific Ocean and travel eastward. The region receives 80-90% of its annual precipitation from May through September (Vimeux, et al., 2009).
The location of Tupungatito glacier makes it particularly suitable for preserving a record of anthropogenic activity in this region. It is located about 100km eastward from a major urban center (Figure 3.1a), Santiago, the capital of Chile, population 5.6 million. Tupungatito glacier and other surrounding glaciers are the main source of water for the capital and the surrounding region (Vimeux et al., 2009). Regional anthropogenic activities, such as industry, agriculture, mining, construction, and large-scale land use release heavy metals and toxic trace elements into the environment, greatly increasing natural background levels. However, specifics associated with timing, transport, and deposition of the pollutants are not well understood (Lapere et al., 2021).

Ice core analysis captures not only the local effects of human activity, but also regional and in some cases broader scale atmospheric chemical changes. South American emissions of heavy metals have been increasing as a result of increasing population, mining, metallurgical processing, industrial production and agriculture (Eichler et al., 2015; Nriagu & Davidson, 1985; Pacyna & Pacyna, 2001). In Chile and Argentina, the primary source of heavy metals and trace elements in the atmosphere has been the dust emitted during surface mining and milling operations (Hong et al., 2004; Romo-Kröger et al., 1994).

This study reports on the analysis of major and trace elements from an ice core recovered from Tupungatito Glacier in the Central Chilean Andes. Glaciochemical and isotopic analyses of TPG-12 indicate that the record is well preserved (see section 2.2 for more details). The ice core is sub-annually dated based upon seasonal peaks in multiple dust elements (La, Pr, V, Mg, & K) and $\delta^{18}$O. We subsequently compared the dated ice core record to global climate reanalysis datasets.
Figure 3.1 (a) Map showing mean June-August 250 hPa wind speed in m/s (1981-2010 climatology) with inset location map for Tupungatito core site. Wind map created using the Climate Change Institute’s ClimateReanalyzer.org (CCI, 2021). Original data source is monthly ERA-Interim reanalysis (Dee et al., 2011; ECMWF 2022). (b) Aerial image of Tupungatito Glacier with indicated drill site (red dot) and Tupungato volcanic complex with fumarolic fields (yellow) (Benavente et al., 2013).

To determine the long-term climatological setting (e.g., 2m-temperature and precipitable water) at the ice core site, we utilized annual means of the ECMWF European Reanalysis of the 20th Century (Poli et al., 2015) (ERA-20C; ECMWF, 2021b) reanalysis dataset with 1.25° x 1.25° grid cell resolution. We chose ERA-20C because its 1900-2010 record period is comparable to that of TPG-12. Timeseries data were extracted from ERA-20C at the gridcell registered to the latitude/longitude coordinates of the ice core site (33.41S, 69.81W). Temperature and precipitable water annual mean anomalies were calculated based on the 30-year 1981-2010 climate normal.

From this initial analysis, we find a subtle shift towards warmer temperatures starting around 1968 and continuing up to year the ice was recovered (Figure 3.2a). The spatial distribution
of temperature anomalies also indicates two nodes of enhanced temperature increase over the central Andes (southern Peru, western Bolivia, and northern Chile) and over Patagonia. However, the warming trend over the Tupungatito ice core site is relatively modest in the reanalysis data (Figure 3.3a). Using the same climatology, we do not observe significant changes in precipitable water (Figure 3.2b) in the annually averaged ECMWF ERA-20C data from the same grid point. Spatially, ECMWF ERA-20C captures an increase in precipitable water over the Amazon Basin and a slight decrease over northern Argentina, but no change is observed in the Tupungatito ice core site grid point (Figure 3.3b).

Figure 3.2. ERA-20C annual 2m-temperature (a) and precipitable water (b) anomalies for site TPG-12. The anomalies are based on the 1981-2010 climate normal.
Figure 3.3. Maps showing ERA-20C annual 2m-temperature (a) and precipitable water (b) anomalies for the period 1905-1980 compared to the 1981-2010 climate normal. Maps created using ClimateReanalyzer.org (CCI, 2021).

3.2. Methodology

3.2.1. Ice Core Collection and Physical Features

In February 2012, a 61m deep ice core (TPG-12) was recovered by our joint Chilean-US team at the Tupungatito Glacier (5603m, 33°24’S, 69°48’W). The glacier is located in the caldera of the actively outgassing Tupungatito Volcano, in Maipo Valley in the Central Chilean Andes. The outgassing from Tupungatito’s active fumaroles is constant and in general the gases are blown downslope and away from the drill site. The continuous 61m core consisting of 98 sections was collected in the field using a 3-inch diameter StampfliTM aluminum electromechanical drill. To ensure that surface melting did not impact results, borehole temperatures were measured. They ranged from -10.5°C at the bottom (61m) to -15.5°C (approximate mean annual temperature) at 10 m below the ice surface. Minimum 2020 2m winter temperature measured by an AWS (installed
in 2019) located 500m away from the drill site at 5575m a.s.l. was -32°C and the maximum recorded 2m wind speed over that same time period was 172 km/hr. Field and laboratory observations of the TPG-12 ice core reveal 85 distinct melt features with the thickest up to 31 cm (Figure 3.4.). Visible melt layers occur throughout all seasons, but only occur sporadically from year to year and primarily since the 1950s. It should be noted that melt layers are more-easily distinguished in the upper part of the core where the average density is lower.

However, isotope values do exhibit higher (potentially warmer) peaks starting around 1948, but this may be an unintended consequence of sampling resolution, notably smoothing of the seasonal signal due to thinning of annual layers and potential stable isotopic diffusion closer to the bottom of the core.

![Figure 3.4.](image)

**Figure 3.4.** δ¹⁸O (‰) record with melt layers indicated in blue

The ice core was packed into clean, heavy duty poly tubing for frozen transport to the Climate Change Institute ice core facility. To prevent contamination from the drilling process, the ice core sections were divided into ~10cm-long pieces using a clean ceramic knife under a HEPA
clean hood housed in a dedicated freezer at -20°C. Each 10cm ice core section was decontaminated by removing the outer ~5mm layer using a DI-cleaned ceramic knife and a clean plastic ice core lathe. Subsequently, each decontaminated section was split. One half was used for stable isotope measurements and the other for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis. Each dedicated ICP-MS ice sample was transferred directly into an acid-cleaned (using 10% trace metal grade HNO3) 120ml, polypropylene Sarstedt jar for trace element analysis. Our collection and sampling methods closely follow the procedures presented in Potocki et al., (2016). Chemical measurements follow the procedure described in Osterberg et al., (2006) and Potocki et al., (2016) (see section 2.3).

3.2.2. Dating of the Ice Core

Annual net mass balance at the Tupungatito Glacier drill site, calculated using annual layer thickness and density measurements, ranges from a minimum of 0.18 m w.eq. to a maximum of 0.97 m w.eq. and is on average 0.48 m w.eq. for the entire length of the ice core record (~100 years), similar to previous studies conducted in this region of the Andes, (Bolius et al., 2006). Sampling yielded on average 6.6 samples/year. We used the CCI Ice Core Dating software to develop the TPG-12 depth-age scale. The TPG-12 depth-age scale is based on annual layer counting of well-preserved seasonal signatures in the stable water isotope δ18O record (Figure 3.5.), with the highest and lowest values representing the summer and winter respectively. The seasonal isotope signal supports seasonal signatures in crustal dust element concentrations (Wedepohl, 1995) (e.g. La) characterized primarily by austral spring/summer peaks. The age estimate for the ice core is ~100 years (1913-2012) based upon counting of the annual layers in isotopes and dust element chemistry (La, Pr, V, Mg, & K). Each annual layer was determined and
agreed upon by four independent ice core dating experts, resulting in an estimated counting error of +/- 1 year.

Figure 3.5. Example of annual layer signal based on La concentration (ng/L) and $\delta^{18}O$ (‰) from the upper (a) and lower (b) part of TPG-12 ice core.
3.2.3. Chemical Analysis

TPG-12 stable water isotope samples were analyzed for oxygen isotopes in vapor using a Picarro Laser Cavity Ringdown Spectrometer (Model L2130-i) with a high throughput vaporizer using the SMOW standard. Thawed TPG-12 ICP-MS samples were acidified to 1% with Optima double-distilled HNO3 under a class-100 HEPA clean bench and left to digest for 60 days at room temperature for major and trace element analysis (Sr, Cd, Cs, Ba, Pb, Bi, U, As, Li, I, Mn, Fe, Co, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Na, Mg, Cu, Tm, Yb, Lu, Ag, Al, S, Ca, Ti, V, Cr, Zn, and K). Samples were measured using a Thermo Fisher Scientific Element-2 ICP-MS instrument, calibrated daily with certified water reference standards that bracket the expected sample concentration range. Detection limits for major and trace elements are defined as three times the standard deviation of MilliQ (>18.2 MΩ) deionized water-ice blanks from previously prepared ice that was passed through the entire decontamination and sampling process (E. C. Osterberg et al., 2006; Potocki et al., 2016).

3.3. Results and Discussion

3.3.1. Flux vs Concentration

We used the TPG-12 accumulation record to calculate flux (flux = concentration x accumulation rate/per unit area) values for each measured element. We then compared these flux values to the associated concentrations for each element. The observed result indicates no significant difference between the two methods (Figure 3.6.). Therefore, we use concentration data for the remainder of this study.
Figure 3.6. Example of the comparison for selected chemical species concentration and flux values (a) Cu, (b) As, (c) Pb, (d) Ag, (e) Cd.
3.3.2 EOF Analysis

We used a principal component analysis method, Empirical Orthogonal Function (EOF) analysis (Mayewski et al., 1994; Peixoto & Oort, 1992) to compare multiple analyses simultaneously providing an organized description of the similarities and differences among them (Meeker et al., 1995). EOF analysis is a mathematical decomposition of a data set in terms of orthogonal basis functions (EOF modes) determined from the data. EOFs are designed to capture temporal variance using as few modes as possible. We ran the EOF using all 38 chemical species and $\delta^{18}O$. We show the decomposition of the first ten EOFs as these are the most significant, as indicated by the Total Variance Explained (TVE). EOF analysis of TPG-12 chemistry data is used to reveal common airmass source associations (Table 3.1.). Using this approach, we interpret EOF 1 as a mainly atmospheric dust signal because it is composed of all the crustal elements measured (69% TVE). EOF 1 also accounts for more than 90% of the total signal of all analyzed rare earth elements. We interpret EOF 2 as an anthropogenic pollution signal because it contains elements typically associated with human industrial activity – Cd, Pb, Ag, Cu and Zn (8% TVE) in addition to 23% of the $\delta^{18}O$. The remaining pollution signal is captured by EOF 4 (4% TVE) representing 34% of total Cd and 22% of total Zn. EOF 3 (5% TVE) representing 37% of total S, 27% of total Ca and negative 25% of total Bi. Because of the inverse association of Bi with S and Ca, we do not interpret EOF 3 as a volcanic signal but rather as a gypsum dust signal. EOF 5 (2% TVE) and EOF 7 (2% TVE) represent 26% and 25% of the total Zn, respectively. EOF 6 (1.9 % TVE) captures 44% of the $\delta^{18}O$ and likely represents the variation in temperature of the annual precipitation. EOF 8 (1% TVE) represents 30% of total Cr and EOF 9 (1% TVE) represents 16% of the total Ba. EOF 10 (1% TVE) represents 17% of the total I. The fact that human source
pollutants are represented by several EOFs demonstrates multiple sources, including, for example, general industry in the Santiago region, mining, and smelting.

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**Table 3.1.** EOF table of trace elements and $\delta^{18}$O as measured in the TPG-12 samples. The numbers in the table represent the percent of variance associated with each major element and $\delta^{18}$O.
3.3.3. Stable Water Isotope $\delta^{18}O$

The $\delta^{18}O$ stable water isotope record exhibits a well-preserved seasonal signal throughout the length of the TPG-12 ice core record (Figure 3.4.). However, values before 1930 display less seasonal variability compared to the rest of the core – likely a consequence of sampling resolution as noted earlier. Seasonal values range from -30.6 ‰ (winter, colder) to -11.6 ‰ (summer, warmer) with an overall mean value of -22.5 ‰. We do not see any significant trends in the isotopic record despite apparent trends in the temperature record as shown by annually averaged 2m temperature data from the ECMWF ERA-20C reanalysis dataset (Figure 3.2.). Moreover, $\delta^{18}O$ record is not well correlated with the Pacific Decadal Oscillation Index or Multivariate El Niño Southern Oscillation Index, with values -0.21 and 0.21, respectively.

3.3.4. Crustal Enrichment Factors

To understand potential sources for the trace elements in the TPG-12 ice core, we present enrichment factor (EF) calculations using the chemical concentration data. We calculate average crustal enrichment factors (EFc) for each element (Figure 3.7.) using mean upper crust elemental abundance values (Wedepohl, 1995) according to the following: crustal EF for element x $[EFc(x) = \text{mean}([x/r]_\text{sample}/[x/r]_\text{upper crust})]$, where r = Li, Na, Mg, Al, Sr, Cs, La, and Pr. These eight elements are used to reduce the potential bias inherent from using only a single conservative crustal element (E. Osterberg et al., 2008).
3.3.5. Potential Volcanic Contribution

Historical eruptions of Tupungatito (1925, 1945, 1958, 1959, 1960, 1961, 1964, 1968, 1980 and 1986) did not leave recognizable signatures in our S or Bi concentration and EF records. Moreover, we did not find any ash layers that correspond to these events. It is worth noting, however, that the S and Bi records are highly enriched (~50 & ~20, respectively) relative to crustal concentrations – leading us to conclude that constant outgassing of nearby fumaroles may dominate these two chemistry records (Figure 3.7). An additional fact worth noting is that the majority of our chemical elements of interest (Cu, As, Pb, & Ag) only show associations with S and Bi in EOF 1 (Table 3.1.), which is identified as a dust signal. A large percentage of the variance explained for Cd, Pb, Ag, & Cu appears in EOF 2 (Table 3.1.), separate from S and Bi. Therefore,
we conclude that Cu, As, Pb, Ag, & Cd concentrations are not strongly influenced by volcanic outgassing.

We calculated potential volcanic contributions of each element of interest (Table 3.2) based upon global quiescent volcanic outgassing values (Hinkley et al., 1999). We made the assumption that no more than 30% of the S was volcanic in origin. If we make the volcanic S percentage higher than 30%, then the potential volcanic contribution of Cd is more than 100% of observed ice core concentrations. Cd is the only element that exhibits a potentially significant impact from Tupungato outgassing.

<table>
<thead>
<tr>
<th>potential % volcanic contribution of:</th>
<th>Cu (%)</th>
<th>As (%)</th>
<th>Cd (%)</th>
<th>Pb (%)</th>
<th>Ag (%)</th>
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<tr>
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<td>15%</td>
<td>1.01</td>
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<td>41.06</td>
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<td>0.48</td>
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<td>1.59</td>
<td>273.76</td>
<td>30.89</td>
<td>38.70</td>
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</table>

Table 3.2. Potential volcanic contribution of Cu, As, Cd, Pb and Ag from assumed % of S from outgassing.

3.3.6. Chilean Environmental Regulations

In 1991, Chile introduced new environmental regulations governing emissions of sulfur dioxide and particulate matter. A new environmental regulation on arsenic emissions was introduced in 1999 (Caldentey & Mondschein, 2003).

Four important actions taken by the Chilean government decreased lead concentration in air and lead concentration levels in human blood: (1) the introduction of unleaded gasoline in 1990, that, according to the 2003 Prevention and Decontamination Plan for the Metropolitan Area of Santiago, approved by Regulation (DS 058/03 Chile 2003) is allowed to have a maximum lead content of 0.013 g/L; (2) the compulsory use of cars with catalytic converters from model year
1992 onwards that prevents the use of leaded gasoline because lead damages the catalytic converter; (3) the approval of a new standard for lead in air (0.5 µg/m³ as annual mean level), legally valid from February 2001 (DS 136/00 Chile 2000); (4) the progressive decrease in lead content in leaded gasoline, that was ultimately banned in April 2001 (SESMA Chile 2002), was the main cause of the decrease in urban lead pollution (Tchernitchin et al., 2006).

Additionally, we perform Hysplit back-trajectory (84 hours) cluster analysis for selected years and different seasons. The cluster analysis results (Figure 3.8) show that the majority of the air masses reaching the TPG-12 drill site are coming from the west and northwest.

![Figure 3.8](https://www.ready.noaa.gov)

**Figure 3.8.** Example Hysplit maps with backward trajectories for Austral summer 2007/2008 (a) and winter 2009 (b), generated on https://www.ready.noaa.gov.
3.3.7. Highly Enriched Anthropogenic Pollutants

Elements with EFc values higher than 10 are considered highly enriched (Duce et al., 1975; Planchon et al., 2002a; Vallelonga et al., 2004). In this section we focus on the potential anthropogenic pollutants that are highly enriched relative to natural levels: As, Pb, Cu, Ag, and Cd (Figure 3.9.).
Figure 3.9. Variation in crustal enrichment factor values through time for the elements Cu, As, Pb, Ag and Cd respectively. The thinner and lighter color lines represent unsmoothed enrichment factor data. Thicker and darker color lines are annually averaged enrichment factor values. There is no historical emissions data available for As, Cd and Pb pollution over this time period. Chilean Cu and Ag mine production – thick black lines, (Source: USGS, 2014; COCHILCO, 2015). The shaded area indicates the period of environmental regulations.

3.3.7.1. Copper (Cu)

Concentrations of Cu range from 21.6 to 18,085 ng/L, with a mean value of 1,760 ng/L (Table 3.3a). EFc values for Cu range from 3.9 to 508, with a mean value of 40 (Table 3.3b). Concentrations of Cu exhibit peak values of ~6000 ng/L from 1913 to 1970. After 1970, Cu concentration peak values increase significantly with many above 12,000 ng/L (Figure 3.9.). Similar to As and Pb, the Cu record exhibits a period with extended reduction in concentration during the late 1930’s.
Figure 3.10. Variation in concentration values through time for the elements Cu, As, Pb, Ag and Cd respectively. The thinner and lighter color lines represent unsmoothed data. Thicker and darker color lines are annually averaged values. The shaded area indicates the environmental regulations period.
Table 3.3. a) Minimum, maximum and mean concentration value of analyzed elements and $\delta^{18}$O and, b) Minimum, maximum and mean crustal enrichment factor value of analyzed elements.

Cu EFc values (Figure 3.10.) are relatively low from 1913 to 1935 with a brief small peak from 1927 to 1930. In 1935, values increase sharply and remain high until 1980 whereupon they increase further until 1990. Cu EFc values then drop back down to pre-1980 levels by 1997. Between 1997 and 2004 there is a large peak centered around 1999, values then increase steadily till the end of the record in 2013. Chilean Cu production (Figure 3.10.) was low from 1900 until the early 1920’s, production then experienced a brief period of increased activity between 1925 and 1930, before dropping back down to 1920 levels again.

Starting in the early 1930’s, after a brief and dramatic drop, Chilean Cu production underwent a significant increase, levelling-out around 1937 and remaining high until the mid-1950’s (Figure 3.9.). Starting in the mid-1950’s, the rate of Chilean Cu production increased

### Table 3.3

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<th>Maximum</th>
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**Concentrations**

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**EFc**

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steadily until the mid-1970’s at which point it nearly doubled until the early 1990’s. Starting in the early 1990’s, the rate of Chilean Cu production more-than tripled up until 2010 (USGS, 2014; COCHILCO, 2015).

The TPG-12 ice core Cu EFc record captures most of the significant features during the historical rise of Chile’s Cu production. It is interesting to note, however, that the ice core record shows a steady reduction in Cu EFc values between 1990 and 1997, precisely when Chilean Cu production was undergoing its most dramatic increase. This discrepancy could be explained by the 1991 environmental regulations governing emissions of particulate matter and demonstrates that they were effective, at least up until 1997. However, by 1999 emissions from Chilean Cu production eclipse the environmental regulations and Cu EFc values peak in the ice core record. A second round of environmental regulations enacted in 1999 reflects the Cu EFc decrease from 1999 to 2004. A large Cu EFc peak occurs from 2007-2008 and a similarly timed peak occurs in many of the TPG-12 EFc records. The 2007-2008 EFc peak may be related to local volcanic activity, perhaps an increase in outgassing, as indicated by the biggest S and Bi spikes in the entire record (Figures 3.11.). The 2007-2008 EFc peak likely obscures the anthropogenic signal in this part of the TPG-12 Cu EFc record. However, based upon the high Cu EFc values observed after 2008, rapidly increasing Chilean Cu production appears to overpower environmental regulations designed to limit pollution from the Cu mining and smelting process (Caldentey & Mondschein, 2003).
Figure 3.11. Concentration values for all elements used in this study. Black lines are raw data and the red lines are annual data.

3.3.7.2. Arsenic (As)

Concentrations of As range from 5.4 to 11.6 ng/L, with a mean value of 963 ng/L (Table 3.3a). EFc values for As range from 18 to 1,774, with a mean value of 137 (Table 3.3b). As is highly enriched for the entire length of the record. Concentrations exhibit relatively consistent variability throughout the length of the record (Figure 3.10.). However, two periods stand out with extended reductions in concentration, the first from 1935 to 1940 A.D. and the second from 2003 to 2012 A.D. EFc values for As display a steady increase from 1913 up to 1970 (Figure 3.9.), followed by a significant increase from 1970 to 1975, then a significant drop back down to 1970 levels by 1979. By 1980, EFc values sharply increase and remain high until 1993, whereupon they begin a steady decline until 2003.
In 1991, new environmental regulations governing emissions of sulfur dioxide and particulate matter were introduced in Chile to cut down on pollution from copper (Cu) mining and smelting and more specific regulations for As emissions were introduced in 1999 (Caldentey & Mondschein, 2003). We see a steep decline in As EFc values starting in 1999 and lasting until 2003 whereupon the trend reverses. Starting in 2003, EFc values steadily increase up until the end of the record with a large peak in 2007-2008. As previously mentioned, the 2007-2008 As EFc peak may be related to local volcanic outgassing because there are no published reports of a Tupungatito eruption at that time. It is likely that rapidly increasing Chilean mining activity is responsible for the observed rise in As from 2003 to the end of the record and the associated rise in Cu over the same time period.

3.3.7.3. Lead (Pb)

Concentrations of Pb range from 0.11 to 9,563 ng/L, with a mean value of 553 ng/L (Table 3.3a). EFc values for Pb range from 0.35 to 61, with a mean value of 7.3 (Table 3b). Concentrations of Pb exhibit relatively consistent variability and values throughout the length of the record (Figure 3.10.). However, similar to the As record, two periods stand out with extended reductions in concentration, the first from 1935 to 1940 A.D. and the second from 2003 to 2012 A.D.

EFc values for Pb display a steady increase from 1913 up to 1993. Starting in 1993, Pb EFc values decrease steadily until 1999 whereupon they flatten out and remain close to 1913 values for the remainder of the record, apart from the large peak in 2007-2008 (Figure 3.9.). The steady Pb decrease that we observe through the 1990’s coincides with Chilean government actions undertaken to reduce the Pb concentrations in the air and in the blood levels of the population including: 1) introduction of unleaded gasoline in 1990; 2) compulsory use of cars with catalytic converters from 1992 models onwards; 3) progressive decrease in the lead content of leaded
gasoline; and 4) new standards for the allowable concentration of Pb in air, effective 2001 (Tchernitchin et al., 2006). The annual usage of unleaded gasoline eclipsed that of leaded gasoline around 1996-1997 and by 2000, the annual usage of unleaded was more than three times that of leaded (SESMA Chile, 2001). Leaded gasoline was finally banned in April 2001 (SESMA Chile, 2002). Fossil fuel combustion data for Chilean electrical generation (Gaete-Morales et al., 2019) exhibits consistent growth in usage since the 1990’s. This increasing trend is not reflected in our ice core chemistry data. Therefore, we do not believe that Chilean electrical generation is responsible for our observed Pb signal.

3.3.7.4. Silver (Ag)

Concentrations of Ag range from 0.08 to 23.81 ng/L, with a mean value of 2.25 ng/L (Table 3.3a). EFc values for Ag range from 0.69 to 3070, with a mean value of 25.68 (Table 3.3b). Concentrations of Ag are low (~0 to 3 ng/L) between 1913 and 1945 and exhibit low variability (Figure 3.10). Similar to Cu, As, and Pb, the Ag record has an extended period of low concentration during the late 1930’s. Beginning in 1946, Ag concentrations more than double and variability increases dramatically. Ag concentrations and variability remain high for the rest of the record.

Ag EFc peak values are below 10 from 1913 to 1935 with a brief peak above 10 in 1928 (Figure 3.9). In 1935, Ag EFc peak values increase sharply and reach a value of 200 by 1939. Ag EFc peak values then drop slightly but remain high, peaking between 20 and 100, until 1990 whereupon they decrease steadily to a low value of ~10 in 2002. From 2003 to 2013, Ag EFc values increase steadily from ~10 to 30 and are punctuated by a large peak in 2007-2008. As mentioned previously, the 2007-2008 Ag EFc peak is likely related to local volcanic outgassing activity.
Comparison of Ag EFc values to Chilean silver mine production (Figure 3.9.) reveals similarities and some disparities. For example, there is no steady rise in EFc from the mid-1940’s to 1990 and conversely, no steady decline in Ag production from 1990 to 2002, although this may be a result of Chilean anti-pollution legislation. These disparities are likely caused by the fact that the majority of the Ag mines are located far to the north of the TPG-12 ice core site. However, the fact still remains that Ag EFc values are highly enriched for the majority of the TPG-12 record (1935-2013).

3.3.7.5. Cadmium (Cd)

Concentrations of Cd range from 0.23 to 1509 ng/L, with a mean value of 13.27 ng/L (Table 3.3a). EFc values for Cd range from 1.54 to 763, with a mean value of 39.51 (Table 3.3b). Concentrations of Cd vary in a similar fashion ($r = 0.72$, $n = 97$) to those of Cu (Figure 3.10.). Cd EFc values also vary similarly ($r = 0.68$, $n = 97$) to those of Cu (Figure 6). Cd is also associated with Cu in EOF 2, representing 30.8 and 30.7 of their respective variance totals, suggesting that at least a portion of the Cd pollution is a by-product of Chilean Cu mining activities.

3.4. Conclusions

The dust signal peaks during the drier and warmer summer season, based upon timing inferred from the stable water isotope record. Trace metal crustal enrichment analysis reveals an increase in emissions of heavy and trace metals (As, Cu, Ag, Pb, and Cd) to the atmosphere from human activities in this region of South America during the last 70 years. As, Cu, Ag, and Cd in the TPG-12 ice core are primarily related to anthropogenic mining activities, as previous research also shows (Hong et al., 2012; Planchon et al., 2002b; Schwanck et al., 2016). Pb in the TPG-12 ice core is associated with emissions from leaded gasoline (Eichler et al., 2015; Tchernitchin et al., 2006a).
In all five of the anthropogenic source elements discussed here (As, Cu, Ag, Pb, and Cd), the pronounced decrease in EFc observed during the 1990’s is most-likely a direct result of Chilean environmental legislation enacted to control air pollution. The observed decrease suggests the pollution regulations were effective, at least up until the early 2000’s, at which point there is a steady EFc increase (punctuated by a possible large volcanic-related peak in 2007-2008) in all the aforementioned elements. This suggests that further legislation is required to control air pollution caused by increased mining and production.
CHAPTER 4
SOUTH GEORGIA ICE CORE RECONNAISSANCE


4.1. Introduction

The study of past climate based on ice cores has been largely developed from the polar regions and more recently in high-elevation mountain areas. However, a gap still remains in the sub-Antarctic zone, where a few islands, some supporting glaciers, punctuate an otherwise uninterrupted expanse of open-ocean. Ice cores from these locations provide a unique opportunity to capture atmospheric chemistry and atmospheric circulation of Southern Ocean.

The longest and most complete meteorological records for the Southern Atlantic region are from Grytviken meteorological station, South Georgia Island (54º S, 36º W) and Orcadas meteorological station, Laurie Island (61º S, 45º W). These meteorological records begin 1905 and 1903, respectively, and the associated temperature measurements show a warming trend, with an average rate of 0.13°C decade\(^{-1}\) at Grytviken, and 0.2 °C decade\(^{-1}\) at Orcadas (Thomas et al., 2018; Turner et al., 2005). A similar warming trend is reported for King George Island, South Shetland Islands on the west side of the Antarctic Peninsula (Angiel et al., 2010). Moreover, an increase in annual mean wind speed, precipitation and cloudiness has been observed in South Western Atlantic region (Jones et al., 2016). For example, at Grytviken an increase in precipitation (45 mm decade\(^{-1}\)) is noted for the period 1907-2016, and mean annual precipitation of 1,590 mm is found over the climatological period 1951-1980 with the highest precipitation totals in March–May (MAM) and June–August (JJA) (1905-2016) (Bannister & King, 2020; Z. Thomas et al., 2018; Van Den Broeke, 2000; Yan et al., 2005). Sub-Antarctic atmospheric circulation, on inter-annual
to decadal timescales, is dominated by the interaction of the Southern Annular Mode (SAM), the Antarctic Circumpolar Wave (ACW), and the El Niño-Southern Oscillation (ENSO) (Mayewski et al., 2016; Thompson & Solomon, 2002).

South Georgia is the largest of the sub-Antarctic islands. Due to its location, south of the marine polar front and within the west to east atmospheric flow in the mid-latitude Southern Hemisphere (~54 °S), the island is an important and potentially rare site for obtaining past climate records (Figure 4.1.). Unfortunately, South Georgia glaciers are retreating in response to modern warming (Farías-Barahona et al., 2020; Graham et al., 2017) making ice core retrieval at this site a critical priority.

![Map showing the location of South Georgia](image)

**Figure 4.1.** Yellow arrow indicates location of South Georgia directly in the path of the westerlies (orange region). Map created using ClimateReanalyzer.org (CCI, 2021).
4.2. Ice Core Chemistry

In October 2015, a continuous 15.4 m snow/firn core (SG-15), consisting of 29 sections, was recovered by our team from a site in central South Georgia. The core was drilled using a 2-inch diameter Stampfli Electromechanical Ice Core Drill. Based on surface glacier morphology the drill site was selected on the divide between the Briggs and Esmark Glaciers at ~850 m a.s.l. (54°11’23”S, 37°5’43”W). The core was recovered in excellent condition and contained some melt layers (Figure 2) mostly below 7 m in depth. The thickest melt layers are located in the warmest part of the core, between the measured borehole temperatures of -0.4 °C at 6 m depth and -0.5 °C at 10 m depth. Borehole temperatures range from -1.8 °C at 4 m depth to -1.5 °C at the bottom with a peak of -0.4 °C at 6 m depth (Figure 2).

The thickest melt layers are located in the warmest part of the core, between the measured borehole temperatures of -0.4 °C at 6 m depth and -0.5 °C at 10 m depth. Borehole temperatures range from -1.8 °C at 4 m depth to -1.5 °C at the bottom with a peak of -0.4 °C at 6 m depth (Figure 4.2.).
The ice core was processed at the drill site because logistics for this reconnaissance effort did not allow for ice to be returned to the lab in a frozen state. To prevent contamination from the drilling process, the core was cut into ~10 cm sections, and then each section was scraped to remove the outer ~5 mm layer, using a plastic ice core lathe and a clean ceramic knife. Subsequently, each scraped section was split lengthways into two parts. One part was used for trace element analysis and the other for stable isotope measurements. Each dedicated trace element sample was placed into a pre-cleaned (using 10 % trace metal grade HNO₃) 120 ml polypropylene Sarstedt container. Also, each stable isotope sample was transferred to a pre-cleaned (using Deionized Water) 120 ml polypropylene Sarstedt container. Our field sampling protocol closely follows the procedures described in Hooper and others (2019) and laboratory measurements follow the procedure presented in Osterberg and others (2006).

In November 2015, the 162 SG-15 ice core samples were transported to the Climate Change Institute laboratory at the University of Maine, USA. All sample containers remained in cold (4 °C) storage pending analysis. Before analysis, each sample was weighed and acidified to 1 % solution with Optima double-distilled HNO₃ under a class-100 HEPA clean hood and allowed to digest for 60 days. All acidified samples were analyzed for major and trace element concentrations (Sr, Cd, Cs, Ba, La, Ce, Pr, Pb, Bi, U, As, Li, Al, S, Ca, Ti, V, Cr, Mn, Fe, Co, Na, Mg, Cu, Zn, and K) using a Thermo Electron Element 2 ICP-SFMS.

SG-15 stable water isotope samples were analyzed for δD and δ¹⁸O using a Picarro Laser Cavity Ringdown Spectrometer (Model L2130-i) with a high throughput vaporizer using the SMOW

The signal of $\delta^{18}$O from the top ~6 m of SG-15 appears to be well-preserved (considerable variability) with values ranging from -5 ‰ to -15.8 ‰. Below this depth, down to the bottom of the core, $\delta^{18}$O values display less variability compared to the upper part of the core (Figure 2) and range between -6.8 ‰ and -10.1 ‰ and the signal is dampened due to melting. Most of the chemical elements display a similar dampened signal below ~6 m depth (Figure 4.3.). The dampening is a consequence of summer surface melting and water percolation down the profile.

We assume that the dampened signal below ~6 m depth likely represents the previous warm season, 2014/2015. In this case, the upper ~6 m of the core captures the coldest part of the year (~6-7 months of accumulation).
To assess natural versus anthropogenic source for the core chemistry, we conducted enrichment factor (EFc) calculations using mean upper crustal elemental abundance values (Wedepohl, 1995), where EFc(x)=[(x/r)sample/(x/r)upper crust) and r is one of the conservative crustal elements: Ce, La, Pr, or Ti – and the final EFc for element x is the mean result of the calculations from the four conservative elements (Potocki et al., 2016; Potocki, Dixon, et al.,
EFc values higher than 10 are considered to be highly enriched relative to natural crustal levels (Planchon et al., 2002a). Thirteen elements (As, Bi, Ca, Cd, Cu, K, Li, Mg, Na, Pb, S, Sr, and Zn) have EFc values higher than 10, and in some cases higher than 100 (Figure 4.4). Highly enriched elements may still indicate a crustal material source (Duce et al., 1975), but EFc values greater than an order of magnitude above crustal inputs likely indicate the influence of other emission sources (Vallelonga et al., 2004).
Figure 4.4. Crustal enrichment factor (EFc) values by depth for selected SG-15 elements. The orange color indicates values greater than 10 and the red line is a value of 100.

To further distinguish between potential sources of chemical elements deposited at the SG-15 drill site, we employed Empirical Orthogonal Function (EOF) analysis (Matlab R2013b)
The high accumulation at the SG-15 ice core site allows the EOF analysis to be used to distinguish sub-seasonal changes within the record. We ran the EOF using all 26 chemical elements and two stable water isotopes. The first seven EOFs are the most significant, as indicated by the Total Variance Explained (TVE, Table 4.1). EOF 1 (48.6 % TVE) includes most of species and we interpret it as a predominantly atmospheric dust signal. EOF 2 includes marine source and accounts for 21% TVE. It is composed primarily of marine elements such Na, Sr, Mg, Ca, K and S, and demonstrates the significant marine influence impacting South Georgia. EOF 3 (9.2 % TVE) comprises rare earth elements such as La, Ce, and Pr. This EOF is interpreted as dry deposition from a distinct dust source given that it is inversely associated with stable isotopes, while EOF 4 (6.9 % TVE) is dominated almost exclusively by stable water isotopes. We interpret EOF 4 as an indicator of the variation in the temperature of the captured precipitation (Legrand & Mayewski, 1997). EOF 5 (5.1 % TVE) is dominated by Mn and Ti, which are inversely associated with the rare earth dust elements from EOF 3. This likely represents yet another distinct dust source. EOF 6 (3.1 % TVE) contains Cs exclusively (78.8 %), suggesting that Cs reaches South Georgia Island from a singular point source. There are major Cs deposits in Namibia and Zambia, where intermittent mining is known to take place (Butterman et al., 2004). Although the South Georgia record is too short to be certain, previous studies show a high correlation between Cs concentrations in the Antarctic Peninsula and zonal winds in the Southern Africa region (Figure 4.5) (Potocki et al., 2016). EOF 7 (2.3 % TVE) is dominated by Mn alone (42.4 %), suggesting yet another distinct source for this element.
Table 4.1. EOF table of trace elements, δ\textsuperscript{18}O, and δD as measured in the SG-15 ice core samples.

The numbers in each row represent the percent variance for each associated EOF. Deeper red indicates more positive values while deeper blue indicates more negative values.

<table>
<thead>
<tr>
<th></th>
<th>EOF 1</th>
<th>EOF 2</th>
<th>EOF 3</th>
<th>EOF 4</th>
<th>EOF 5</th>
<th>EOF 6</th>
<th>EOF 7</th>
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<td>TVE (%)</td>
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<td>6.94</td>
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<td>Sr (ng/L)</td>
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<td>1.97</td>
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<td>-4.80</td>
<td>-0.09</td>
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<td>Bi (ng/L)</td>
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<td>U (pg/L)</td>
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<td>Al (ug/L)</td>
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<td>S (ug/L)</td>
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<td>-7.78</td>
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<td>2.95</td>
<td>31.08</td>
<td>-5.43</td>
<td>42.38</td>
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<td>4.06</td>
<td>17.28</td>
<td>-0.19</td>
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<tr>
<td>Co (ng/L)</td>
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<td>-6.97</td>
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<td>0.58</td>
<td>9.32</td>
<td>-0.03</td>
<td>-1.07</td>
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<tr>
<td>Na (ug/L)</td>
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<td>Mg (ug/L)</td>
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<td>0.00</td>
</tr>
<tr>
<td>Cu (ng/L)</td>
<td>77.50</td>
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<td>-5.31</td>
<td>-1.18</td>
<td>-0.22</td>
<td>0.39</td>
<td>0.03</td>
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<td>Zn (ng/L)</td>
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<td>-12.18</td>
<td>-5.83</td>
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<td>-0.67</td>
<td>0.12</td>
<td>0.14</td>
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<td>K (ug/L)</td>
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<td>-0.05</td>
<td>-0.01</td>
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<tr>
<td>O-18SMOW</td>
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<td>-13.25</td>
<td>78.57</td>
<td>-4.10</td>
<td>0.24</td>
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<td>H/D SMOW</td>
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<td>-11.06</td>
<td>81.65</td>
<td>-4.21</td>
<td>0.22</td>
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</table>
Figure 4.5. Correlation between mean annual Cs concentrations from Detroit Plateau and (a) annual 10 m U-Wind (NCEP CFSR) and (b) annual 10m U-Wind (ERA 5) for the 1981-2006 period. Maps created using ClimateReanalyzer.org (CCI, 2021)

We also ran EOFs for the upper (0 to 6.2 m depth) versus the lower (6.2 to 15.4m depth) part of the SG-15 ice core to assess the effect of the well-preserved upper section of the ice core versus the dampened lower section (Table 4.2 and 4.3). The results demonstrate that EOF 1 and EOF 2 are represented by the same chemical elements as previously calculated, and therefore we interpret EOF 1 and EOF 2 to represent atmospheric dust and sea spray signals, respectively.
Table 4.2. EOF table of trace elements, δ¹⁸O, and δD measured in the SG-15 ice core from the surface to 6.2m depth. The numbers in each row represent the percent variance for each associated EOF. Deeper red indicates more positive values while deeper blue indicates more negative values.
Table 4.3. EOF table of trace elements, δ¹⁸O, and δD measured in the SG-15 ice core from the 6.2 to 15.4m depth. The numbers in each row represent the percent variance for each associated EOF. Deeper red indicates more positive values while deeper blue indicates more negative values.

<table>
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<tr>
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<th>EOF 2</th>
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<tr>
<td>TVE (%)</td>
<td>36.73</td>
<td>16.81</td>
<td>8.43</td>
<td>6.77</td>
<td>5.26</td>
<td>4.05</td>
<td>3.57</td>
<td>3.22</td>
</tr>
<tr>
<td>Sr (ng/L)</td>
<td>24.50</td>
<td>66.75</td>
<td>-0.41</td>
<td>-4.17</td>
<td>-0.23</td>
<td>0.18</td>
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</tr>
<tr>
<td>Cd (ng/L)</td>
<td>0.13</td>
<td>-1.12</td>
<td>9.96</td>
<td>-14.37</td>
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<td>-0.49</td>
<td>15.17</td>
<td>48.47</td>
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<td>Cs (ng/L)</td>
<td>37.38</td>
<td>-4.77</td>
<td>-3.05</td>
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<td>0.58</td>
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<tr>
<td>Ba (ng/L)</td>
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<td>4.97</td>
<td>-0.01</td>
<td>-3.06</td>
<td>2.33</td>
</tr>
<tr>
<td>Ce (ng/L)</td>
<td>80.07</td>
<td>-2.03</td>
<td>-5.83</td>
<td>-3.16</td>
<td>1.41</td>
<td>0.02</td>
<td>-2.61</td>
<td>0.52</td>
</tr>
<tr>
<td>Pr (ng/L)</td>
<td>78.48</td>
<td>-1.93</td>
<td>-5.69</td>
<td>-3.69</td>
<td>3.17</td>
<td>0.00</td>
<td>-2.79</td>
<td>0.99</td>
</tr>
<tr>
<td>Pb (ng/L)</td>
<td>22.43</td>
<td>-4.64</td>
<td>1.97</td>
<td>-3.07</td>
<td>10.68</td>
<td>-0.24</td>
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<td>-2.58</td>
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<td>-24.74</td>
<td>0.13</td>
<td>-7.46</td>
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<td>U (pg/L)</td>
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<td>-3.43</td>
<td>-14.61</td>
<td>1.56</td>
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<td>-1.03</td>
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<td>As (ng/L)</td>
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<td>3.03</td>
<td>-0.83</td>
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<td>7.73</td>
<td>0.00</td>
<td>1.04</td>
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<tr>
<td>Li (ng/L)</td>
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<td>0.03</td>
<td>0.00</td>
<td>4.58</td>
<td>-3.50</td>
<td>0.08</td>
<td>1.93</td>
<td>0.32</td>
</tr>
<tr>
<td>Al (ug/L)</td>
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<td>-0.01</td>
<td>0.15</td>
<td>0.66</td>
<td>-0.03</td>
<td>0.00</td>
<td>-0.23</td>
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<tr>
<td>S (ug/L)</td>
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<td>82.42</td>
<td>-0.42</td>
<td>-2.82</td>
<td>-2.00</td>
<td>0.68</td>
<td>0.15</td>
<td>0.07</td>
</tr>
<tr>
<td>Ca (ug/L)</td>
<td>6.96</td>
<td>7.31</td>
<td>25.05</td>
<td>-7.55</td>
<td>-5.09</td>
<td>-11.34</td>
<td>-9.19</td>
<td>3.20</td>
</tr>
<tr>
<td>Ti (ng/L)</td>
<td>70.97</td>
<td>-5.93</td>
<td>0.42</td>
<td>3.57</td>
<td>-2.21</td>
<td>0.00</td>
<td>-0.29</td>
<td>-0.36</td>
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<td>V (ng/L)</td>
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<td>-5.63</td>
<td>0.41</td>
<td>4.85</td>
<td>-1.98</td>
<td>-0.45</td>
<td>0.31</td>
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<tr>
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<td>28.14</td>
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<td>-2.09</td>
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<tr>
<td>Mn (ng/L)</td>
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<td>0.46</td>
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<td>0.00</td>
<td>4.32</td>
<td>1.67</td>
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<td>Fe (ug/L)</td>
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<td>-7.24</td>
<td>0.89</td>
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<td>-1.25</td>
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<td>Mg (ug/L)</td>
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<td>1.05</td>
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<td>-0.84</td>
</tr>
<tr>
<td>Zn (ng/L)</td>
<td>5.33</td>
<td>-0.01</td>
<td>61.20</td>
<td>-4.18</td>
<td>-0.30</td>
<td>12.82</td>
<td>-2.95</td>
<td>-0.24</td>
</tr>
<tr>
<td>K (ug/L)</td>
<td>19.49</td>
<td>69.85</td>
<td>-2.09</td>
<td>-1.30</td>
<td>-0.93</td>
<td>0.22</td>
<td>0.41</td>
<td>-0.01</td>
</tr>
<tr>
<td>O-HDMSOW</td>
<td>8.23</td>
<td>16.70</td>
<td>11.66</td>
<td>28.31</td>
<td>26.54</td>
<td>-1.08</td>
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<td>1.15</td>
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<td>H/DSMOW</td>
<td>9.01</td>
<td>21.96</td>
<td>10.11</td>
<td>30.76</td>
<td>20.74</td>
<td>-2.61</td>
<td>0.28</td>
<td>0.79</td>
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4.2.1. Future Site Selection

We used ECMWF European Reanalysis version 5 (ERA5) data to determine estimated maximum annual freezing heights at the SG-15 drill site from 1950 to present (Figure 4.6.). From 1950 to 1970 the freezing height was about 400 m a.s.l., and approximately 600 m a.s.l. from 2000 to 2020. During this most recent period the absolute maximum freezing height was 650 m a.s.l.,
registered in 2021. However, an examination of monthly freezing heights indicates maximum values reaching \(~1250\ \text{m\ a.s.l.}\) or slightly higher at the end of the austral summer (Figure 4.7). The absolute maximum freezing height at the SG-15 drill site in the 72-year ERA5 record is 1889 m a.s.l., attained in March 2000.

![Annual Freezing Height](image)

**Figure 4.6.** ECMWF ERA-5 (0.25 x 0.25 degree) annual mean freezing height (m) for site SG-15. Plotted using Climate Reanalyzer™.
Due to poor weather conditions and time constraints, our original goal to recover an ice core at ~1000 m a.s.l. elevation on either Esmark Glacier or Kohl Plateau was not achieved. Final field operations were instead restricted to ice coring at the divide between the Briggs and Esmark glaciers. Based upon the SG-15 ice core data, we know that any other potential ice core sites on South Georgia Island located at 850 m a.s.l. or below are subject to significant surface melting and associated chemical record loss (Figure 4.8a). The ERA5 monthly freezing height estimates in Figure 6 indicate that a site located above 1250 m a.s.l. may offer more suitable conditions for ice core recovery. Thus, viable drilling sites may be limited to the highest areas of the Lancing Glacier, Christophersen Glacier and the Mount Paget (2934 m a.s.l.) area, Novosilski Glacier and Herz Glacier between Mount Patterson (2195 m a.s.l.), and Mount Carse (2331 m a.s.l.) (Figure 4.8b).
GPR field readings conducted during our field season indicate an ice depth greater than 400 m at the SG-15 drill site, confirming the ice thickness calculations of Cooper and others (2012), and demonstrating potential for a relatively long environmental record. Based upon the findings of Mayewski and others (2016) deeper sections of South Georgia ice still contain well preserved environmental records, as demonstrated by their identification of “annual layers” using ultra-high resolution (120 micron) LA-ICP-SFMS iron and calcium measurements in basal ice from the Fortuna and Nordenskjöld Glacier termini radiocarbon dated at between ~8,600 and ~11,000 years old.

4.3. Conclusions

Paleoenvironmental records from South Georgia Island are needed to provide a baseline for recent and future climate changes in the sub Antarctic and Southern Ocean. Mayewski and others (2016) suggested that sites in the Kohl Plateau region ~1000 m a.s.l. and small ice caps

Figure 4.8. (a) South Georgia with elevations below 850 m a.s.l. shaded in red and (b) below 1250 m a.s.l. shaded in red. 1- Lancing Glacier, 2 - Christophersen Glacier and Mount Paget, 3 - Novosilski Glacier and Herz Glacier. Yellow dot indicates the SG-15 drill site.
above 2000 m a.s.l. could contain well-preserved recent climate records. However, this study demonstrates that significant melting occurs at least up to 850 m a.s.l. during austral summer, and that this elevation is therefore unsuitable for ice preservation and coring. Due to the short time period covered by SG-15, no unambiguous trend or clear seasonality can be determined. However, the fact that there are no prominent melt layers in the upper 6.2 m strongly suggests that the core is derived from winter snow. There is no definitive way to demonstrate the time period represented by SG-15, which could be less than 1 year with many storm events or over multiple years.

Higher-elevation (>1250 m a.s.l.) ice core sites located on glacier plateaus are still likely candidates for well-preserved, continuous modern to past environmental records. Since recovery of an ice core of ~400 m as determined for the SG-15 site requires significant effort and equipment (drilling fluid, a larger camp, more personnel, and all of the associated logistical challenges), future drilling attempts will likely require helicopter support that is at present not permitted or available on South Georgia. Further research on more accessible ice from glacier margins that can be radiocarbon dated offers at least potential for snapshots of past sub Antarctic and Southern Ocean climate.
CHAPTER 5

CONCLUSIONS

Chapters 2-4 of this dissertation provide an overview of the ice core-derived environmental records available from three mountain sites in the Southern Hemisphere.

Chapter 2 (Potocki et al., 2016) of this dissertation focuses on a continuous record of U concentrations in the 27-year long (98 m) 2007 Detroit Plateau (DP-07) ice core. It reveals significant, $10^2$ U concentration increases in the atmosphere since the 1990s related to U mining operations in Australia. Baseline investigations of the distribution of human source pollutants are essential to understand their environmental impact. Very high levels of anthropogenic source pollution from Southern Hemisphere industrial sources, in this case, open pit U mining, are deposited on the northern tip of the Antarctic Peninsula. The impact of U on local ecosystems is yet to be determined, but should now be considered because mean concentration value for 2000s is 7 times higher than WHO safety guidelines (30 µg/L; (WHO - World Health Organization, 2017)). In addition, the DP-07 ice core offers a monitoring basis for assessing changes in Southern Hemisphere source pollutants entering Antarctica.

Chapter 3 (Potocki et al., 2022) is a glaciochemical record from the Tupungatito 2012 (TPG-12) ice core from the Central Chilean Andes with the primary aim of contributing to the understanding of local anthropogenic activities. Chemical analysis shows an increase in emissions of trace and heavy metals (As, Cu, Ag, Pb, and Cd) to the atmosphere from anthropogenic activities in this region of South America since the 1940s. Ag, As, Cd, and Cu in the TPG-12 ice core are mainly related to the mining operations, as previous research has also shown (Hong et al., 2012; Planchon et al., 2002b; Schwanck et al., 2016). In addition, Pb in the TPG-12 ice core is associated with emissions from leaded gasoline (Eichler et al., 2015; Tchernitchin et al., 2006). All,
anthropogenic source elements identified in the TPG-12 ice core display a distinct decrease in enrichment factor values as of the 1990’s illustrating the effectiveness of air pollution and leaded gasoline regulations in Chile. The decrease was effective, at least up until the early 2000’s, at which point there is a steady increase in Cu, As, Pb, Ag, and Cd, indicating that further legislation is required to control air pollution caused by the recent increase in mining and metal production.

Chapter 4 is a study that is focused on the need for paleoenvironmental records from South Georgia as a baseline for recent and future climate changes in the Southern Ocean. A 15.4 m reconnaissance ice core, recovered at 850 m a.s.l. on South Georgia (SG-15), reveals that significant melting can occur at this elevation during austral summer therefore this elevation is unsuitable for preservation of recent years as an environmental archive. Ice core sites located above 1250 m a.s.l. on glacier plateaus are still likely candidates for, continuous, well preserved environmental records, but deep ice core recovery from these locations, requires significant effort and equipment, including advanced logistics with helicopter support that is currently not allowed on South Georgia. Due to the short time period covered by SG-15, no clear seasonality or trend can be determined. There is no absolute way to demonstrate the time period represented by the SG-15 ice core. The record may represent less than 1 year with many storm events or multiple years. However, the fact that there are no prominent melt layers in the upper ~6 m strongly suggests that the core is recovered from recent winter snow. Although the South Georgia record of Cs is too short to be certain it does provide evidence suggesting that Cs reaches South Georgia Island from a singular point source. Previous studies show a high correlation between Cs concentrations in the Antarctic Peninsula and zonal winds in the Southern Africa region (Potocki et al., 2016). Previous studies by Mayewski et al. (2016) suggest that glacier plateaus ~1000 m a.s.l. and small ice caps above 2000 m a.s.l. on South Georgia may still contain well-preserved climate records. In
the same study radiocarbon-dated ice recovered from glacier margins reveals apparent annual layer preservation suggesting that ice recovered from below the recent era of warming likely still contains a well-preserved environmental record.


ECMWF. (2021a). ERA-interim Reanalysis Monthly Means of Daily Means (0.75°x0.75°Degree Latitude/longitude Grid). ECMWF Data Server. https://apps.ecmwf.int/datasets/data/interim-full-moda/.


https://www.osti.gov/biblio/5564219


BIOGRAPHY OF THE AUTHOR

Mariusz Potocki was born on May 16th, 1980, and grew up in Korsze, Poland. He graduated from the University of Warsaw, Poland, where he earned a master’s degree in physical geography in 2004. After graduating, he worked for four years as a geographer/glaciologist for the Polish Academy of Sciences, Department of Antarctic Biology, and took part in three Antarctic expeditions to the Polish Arctowski Antarctic Station on King George Island, South Shetland Islands. At Arctowski Station his scientific interest focused on glacier morphology and cartography of glacial landforms, as well as the rates of glacier movement and deglaciation.

In 2008 Potocki was accepted for the University of Maine Graduate program where he started his doctorate work in the Climate Change Institute under his advisor Dr. Paul Andrew Mayewski. During his studies at the Climate Change Institute, Potocki has participated in ~20 ice core collection field expeditions to South America, Antarctica, Africa, Asia, and Europe. He also holds the record for the world's highest ice core collection – 8050m.a.s.l. His main research interest is in the use of ice core records as proxies for changes in the chemical composition of the atmosphere using state of the art high and ultra-high-resolution analytical methods. He has authored and co-authored 27 peer-reviewed papers, with an additional 2 currently in review.

During his scientific career, he has had the opportunity to cooperate with several international teams of experienced specialists and led expeditions to the Peruvian Andes and South Georgia.

Besides science, Potocki is an adventure-seeker who cherishes traveling, meeting and forging relationships with people and experiencing various cultures. He is also an experienced and award-winning wildlife photographer.
Potocki is a candidate for the Doctor of Philosophy degree in the School of Earth and Climate Sciences at the University of Maine in August 2022.